MICAL
RARY

THIS NUMBER COMPLETES VOLUME XXXI

Volume XXXI June, 1931 Number 6

SOIL SCIENCE

Editor-in-Chief
JACOB G. LIPMAN

Associate Editor
HERMINIE BROEDEL KITCHEN

Contents

The Carbon-Nitrogen Ratio in Relation to the Accumulation of Organic Matter in Soils. FREDERICK J. SALTER..... 413

Phosphorus Assimilation by Soil Microörganisms. L. G. THOMPSON, JR., F. B. SMITH AND P. E. BROWN..... 431

Chemical Methods for Estimating the Availability of Soil Phosphate. P. L. HIBBARD..... 437

The Availability of the Nitrogen in Farm Manure under Field Conditions. A. FLOYD HECK..... 467

Determination of Soil Organic Matter. C. J. SCHOLLENBERGER..... 483

The Modeling of Soils, an Aid in Their Study. R. H. CARR..... 487

Index..... 491

PUBLISHED MONTHLY
THE WILLIAMS & WILKINS COMPANY
MT. ROYAL AND GUILFORD AVENUES
BALTIMORE, MARYLAND, U. S. A.

Made in United States of America

SOIL SCIENCE

FOUNDED BY
RUTGERS COLLEGE
NEW BRUNSWICK, N. J.

ADVISORY STAFF

Prof. A. W. Blair, Dr. J. S. Joffe, Prof. L. L. Lee, Dr. H. C. McLean, Dr. S. Mattson, Prof. A. L. Prince, Dr. J. W. Shive, Dr. R. L. Starkey and Dr. S. A. Waksman, New Jersey Agricultural Experiment Station, New Brunswick, N. J.

CONSULTING EDITORS

DR. F. J. ALWAY
University of Minnesota, St. Paul, Minn.

PROF. K. ASO
Imperial University, Tokyo, Japan

PROF. C. BARTHEL
Central Agricultural Experiment Station, Experimentalfaltet, Sweden

DR. P. E. BROWN
Iowa State College of Agriculture, Ames, Iowa

PROF. DR. ALBERT DEMOLON
Ministry of Agriculture, Paris, France

DR. H. J. CONN
New York State Experiment Station, Geneva, N. Y.

DR. E. B. FRED
University of Wisconsin, Madison, Wis.

DR. J. E. GREAVES
Utah Agricultural College, Logan, Utah

DIRECTOR ACH. GREGOIRE
Agricultural Experiment Station, Gembloux, Belgium

DR. B. L. HARTWELL
26 Rowe St., Auburndale, Mass.

DR. D. J. HISSINK
Soil Science Institute, Groningen, Holland

DR. C. B. LIPMAN
University of California, Berkeley, Calif.

DR. BURTON E. LIVINGSTON
Johns Hopkins University, Baltimore, Md.

DR. T. L. LYON
Cornell University, Ithaca, N. Y.

DR. M. M. MCCOOL
Michigan State College, East Lansing, Mich.

DR. W. H. MACINTIRE
University of Tennessee, Knoxville, Tenn.

DR. E. A. MITSCHERLICH
University of Königsberg, Prussia

PROF. C. A. MOOERS
University of Tennessee, Knoxville, Tenn.

DR. SVEN ODÉN
Central Agricultural Experiment Station, Experimentalfaltet, Sweden

DR. THEO. REMY
Institut für Boden- und Pflansenbaulehre, Bonn a. Rh.

PROF. G. ROSSI
Royal Agricultural High School in Portici, Naples, Italy

DR. E. J. RUSSELL
Rothamsted Experimental Station, Harpenden, England

DR. O. SCHREINER
U. S. Department of Agriculture, Washington, D. C.

DR. ALEXIUS A. J. DE'SIGMOND
Royal Hungarian Joseph University of Technical Sciences, Budapest, Hungary

DR. J. STOKLASA
Technical High School, Prague, Czechoslovakia

PROF. CHAS. E. THORNE
Ohio Experiment Station, Wooster, Ohio

PROF. N. M. TULAIKOV
Agricultural Experiment Station, Saratov, U. S. S. R.

DR. F. WEIS
Royal Agricultural and Veterinary College, Copenhagen, Denmark

PROF. S. WINOGRADSKY
Pasteur Institute, Paris, France

Entered as second-class matter May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879.

Copyright, 1931, The Williams & Wilkins Company

THE CARBON-NITROGEN RATIO IN RELATION TO THE ACCUMULATION OF ORGANIC MATTER IN SOILS[1]

FREDERICK J. SALTER[2]

Ohio State University

Received for publication August 4, 1930

A study of the soil will show that it is a system which is never in a perfect state of equilibrium. It is continually undergoing physical and chemical adjustments with the forces which surround it or are in it. Since these adjustments are never complete, change constantly takes place. One of the most changeable and yet apparently one of the most constant relationships in the soil is that which exists between the soil carbon and the soil nitrogen—the carbon-nitrogen ratio. Many writers have devoted considerable space to organic matter and nitrogen but less has been said in regard to the relation of carbon to nitrogen and the result of various ratios within the soil.

Among the early observations along this line was that regardless of the ratio of carbon to nitrogen in organic materials added to the soil, in a short time the ratio within the soil becomes stabilized at some point near 10 to 1. That this varies somewhat in different localities and at various depths has been shown by several workers. Dyer (14), who gives us one of the earliest observations, studied the carbon-nitrogen ratios of 21 Rothamsted wheat soils at different depths. He found that they varied between 5 and 10 to 1, the surface soils showing a wider ratio than the subsoils. Brown and O'Neal (11) found that, in Iowa, Carrington loam gave a ratio of 12 or 13 to 1, whereas Tama silt loam showed a ratio of 10 to 1. Alway (2) reports that Nebraska soils vary from 11.2 to 13.6:1. Stewart (27) of Illinois states that in general the carbon-nitrogen ratio of the soil tends to become narrower with the aging of the organic material. He found the ratio in the old soils, the gray silt loam, to be 10.4:1; in brown silt loam 12.1:1; and in black clay loam, the younger soil, 11.7:1. Alway and Vail (4) in studying the relative amounts of nitrogen, carbon, and humus in Nebraska soils found that the ratio ran so uniform for surface soils that the carbon content could be estimated with sufficient accuracy from the nitrogen determination. From West Virginia Bulletin 161 it appears that soils of the Huntington series average 13.5:1 carbon-nitrogen ratio whereas those of the Upshur series run 9.8 to 1. The average of the entire state is approximately 11.8 to 1. Ohio soils, from analyses given in by Ames and Gaither (5), average 12 to 1. All of these results indicate that there is some rather stable ratio of carbon to nitrogen for soils of the same region and that the ratio is different in different regions. The factors which most greatly influence the actual ratio are those of climate—temperature and rainfall, the latter as expressed in the ratio R/E, rainfall-evaporation. In regions with a wide rainfall-evaporation ratio and a high temperature there are conditions favorable for luxuriant vegetative growth but at the same time these also favor rapid decomposition processes. Thus, although more organic material may enter into a soil, because of rapid decay it is difficult to keep it.

[1] A thesis presented to the faculty of Ohio State University in partial fulfillment of the requirements for the degree of doctor of philosophy.

[2] The author is indebted to Dr. Firman E. Bear, formerly head of the soils department, Ohio State University, for many helpful suggestions in connection with this work.

Russell (23) shows from his work on Broadbalk plots that it is only by an increase in carbon that nitrogen can be increased in soils. The reverse is also true that without nitrogen carbon will not be held. Therefore in humid sections the carbon-nitrogen ratio tends to narrow down because energetic decay processes cause a more rapid loss of carbon than of nitrogen. In semi-humid sections, those with a rainfall-evaporation ratio of less than 1, we have conditions less favorable for plant growth and for decomposition. The result is that carbonaceous materials do not disappear as readily as do nitrogenous compounds. This tends to widen the carbon-nitrogen ratio. Jenny (16) points out, from his study of climatic factors as related to soil nitrogen, that the total nitrogen content of soils decreases from North to South in the United States in relation to temperature. In the North, with lower temperature, decay slows down and nitrogen is not so readily lost. This permits of an easier maintenance of organic matter in the soil. In the south on the contrary, high temperatures militate against nitrogen accumulation and thus discourage the keeping of organic matter.

Several workers, notably Alway and McLean (3), Blair and McLean (8), and Sievers and Holtz (25), have pointed out that in soil under cultivation the carbon-nitrogen ratio becomes narrower. Stirring the soil appears to produce a much greater loss of carbon than of nitrogen.

When soils are first brought under cultivation there is a rapid loss of organic matter, but as the amount of nitrogen becomes less the rate of loss slows down and the narrower ratio remains fairly stable.

A number of efforts have been made to associate the carbon-nitrogen ratio with the fertility of the soil. Brown and Allison (10) state, "The determination of the carbon-nitrogen ratio in soils is now coming to be considered of much importance in fertility studies. . . . It shows the rate at which decomposition processes are going on in the soil. Experience has shown that if the ratio narrowed beyond a point of about 10 to 1 crop yields may be reduced evidently because of an insufficient production of available nitrogen, phophorus, and potassium. On the other hand, if the ratio was 12 to 1 or above, bacterial activities apparently occur to a satisfactory extent and sufficient amounts of soluble plant-food are produced for good crop growth." From data presented by Russell (23) it appears that if there is any correlation between productivity and the ratio of carbon to nitrogen, fertile soils have the narrower ratio.

Waynick and Sharp (35) have presented data showing the amount of variation found in the total carbon and total nitrogen of California soils. The samples selected were taken for their apparent uniformity and yet the nitrogen fluctuation was as much as 0.977 to 0.21 and the carbon ran from 1.383 to 0.179. As many as 100 samples were taken from plats of a little over an acre. Since these great variations occurred on small areas which appeared to be uniform these authors discredit any significance that might be given to the association of the carbon-nitrogen ratio with soil fertility. Read (22) has corroborated the work of Waynick and Sharp by the study of samples collected from many experiment stations. His analytical results were compared with the actual yields as reported by the various stations.

Although it seems to be impossible to relate the ratio of carbon to nitrogen in soils to the yields to be expected, this ratio appears to be of considerable importance in determining the processes taking place when organic materials are added to soils.

For a long time farmers have realized that the applications of strawy manure or straw alone have a disastrous effect upon the crop yields immediately following. This may also be the result with some green manures, especially when fairly heavy. Many experiments have been carried out to account for this condition. It was soon recognized that the crop failures were due to a lack of available nitrogen. Lyon, Bizzell, and Wilson (18) found that the dried roots of a number of plants brought about nitrate depression. Hutchison (15) found that applications of carbohydrates to soils caused a decrease in soil nitrates. An application of hay dust and straw at once lowered the amounts of ammonia and nitrate, but after several months these became greater. Murray (21), Scott (24), Collison and Conn (12), and others (1, 9, 19, 38), have obtained harmful effects and the depression of nitrates following the use of straw or other cellulosic materials. The early explanation for this decrease in available

nitrogen was that denitrification took place with increased rapidity due to these microörganisms being greatly favored by the material added. This theory was soon replaced by the belief that soil organisms became consumers of nitrogen under certain circumstances and thereby lessened the stock of nitrates. Murray (21) showed that the total nitrogen content of the soil remains the same, following the disappearance of the nitrates, as it was before, indicating a mere change of form. Doryland (13) has probably carried out the most extensive work to show that soil microörganisms may become competitors to crops for the supply of available plant nutrients. He has shown that these competitors are not necessarily "detrimental" organisms, but may be some of the most vigorous ammonifiers. He points out that the most favorable conditions for the consumption of ammonia or nitrates is an application of "energy material," such as carbohydrates or straw. This use of nitrogen by the organisms is simply a normal metabolic process. For the construction of their body tissue they require a certain amount of nitrogen for each unit of carbon consumed. When a substance having a wide energy-nitrogen ratio is added to the soil, since there is an abundance of energy material but very little nitrogen, the organisms make use of the available nitrogen from the soil in their growth processes. Since the soil organisms are more advantageously situated with respect to this nitrogen, the plant suffers.

The work of Brown and Allison (10) agrees with that of Doryland. An application of narrow-ratio materials, such as rotted manure and legume hays, caused increased yields of oats whereas wide-ratio substances lowered the yields.

That the availability of nitrogen following the turning into the soil of organic materials is probably a matter of the carbon-nitrogen ratio is shown by the work of Blair and Prince (9), Wilson and Wilson (38), Thomas and Harper (28) and others. When straws and other residues with a wide ratio are supplemented with legumes or other sources of nitrogen in order to narrow the ratio, no depression of available nitrogen results. If the ratio is sufficiently narrow some nitrate nitrogen is made available. This is shown in the work of Thomas and Harper (28) using straw alone and also supplemented with sources of nitrogen, such as legume hays, nitrate of soda, and sulfate of ammonia. The combination applications brought about larger amounts of available nitrates, because of a narrowing of the carbon-nitrogen ratio.

Waksman (30) has made a thorough study of the microbiological processes connected with the decomposition of organic materials within the soil. He points out that, added to the soil, organic substances are attacked by many forms of microörganisms, including bacteria, actinomycetes, fungi, and possibly protozoa. As a result of these activities the organic tissues are broken down, the available energy is utilized by the organisms, and the inorganic compounds of nitrogen, phosphorus, and potassium are made available for plant growth. Most of the soil microörganisms, with the exception of algae and some autotrophic bacteria, require organic materials as a source of energy. Therefore these substances must become energy sources for soil organisms. The speed with which the materials are decomposed varies considerably. It is not the organic material as a whole that is attacked, but various constituents of this material. Some of these are rapidly attacked whereas others are affected only slightly. Therefore the nature of the composition of the materials added to soils will determine the speed of its decay and the final result of the decomposition. Since in their metabolic processes the organisms synthesize considerable cell substance, and this requires nitrogen and phosphorus, the speed of decomposition will also be governed by the available supply of these elements.

It has been noted by Whiting (36), Whiting and Schoonover (37), Martin (19), Dvorak [cited by Waksman (31)], Waksman (34, 32) and others, that immature green plant materials are decomposed most rapidly, largely because they contain an abundance of water-soluble carbohydrates and nitrogenous compounds. The leaves of plants decompose more rapidly than their stems or roots, because of their higher nitrogen content. As plants become older their carbonaceous materials become transformed to an increasing extent into cellulose and lignins. These latter are decomposed only very slowly.

That the supply of easily available nitrogen is also important in determining the rate of decomposition has been shown by Waksman (31), Waksman and Starkey (33), Anderson (6), Barthel and Bengtsson (7), Merkle (20) and Starkey (26). Materials that are poor in nitrogen but rich in cellulose decompose more slowly than those rich in nitrogen and poor in cellulose. This may be put in other words—materials with a wide carbon-nitrogen ratio decompose more slowly than those with a narrow ratio. In the case of the former, such as straws, corn stover, wood products, and cellulose, the available supply of nitrogen often may become the limiting factor in their decay. Anderson (6) has shown that the rate of cellulose decomposition increases with the increase in available nitrogen until there is sufficient nitrogen for the maximum growth of the microörganisms. He also found that nitrification could take place when cellulose was present, but no nitrates were found until the needs of the bacteria were met. Barthel and Bengtsson (7) also obtained results similar to those of Anderson. They attributed the favorable influence of stable manure upon the decomposition of cellulose in the soil to the available nitrogen present in the manure. When the quantities of manure were doubled the amount of cellulose decomposed was increased proportionately, and halving the amount likewise decreased the decay. Since the same results were obtained with sterilized manure they concluded that the microörganisms present in the manure have no influence in normal soils. They obtained practically the same results with equivalent amounts of ammonium sulfate and ammonium nitrate. Waksman and Tenney (34), working with rye straw, corn stalks, oak leaves, and alfalfa tops, found that the addition of available nitrogen very greatly increased the rate of decay with all the materials except alfalfa. In the latter case adding nitrogen had no effect, as the nitrogen present in the alfalfa was sufficient to bring about a very rapid decay. Thus it appears that narrowing the ratio of carbon to nitrogen causes an increased rate of decomposition with materials having a wide carbon-nitrogen ratio.

Waksman (29) shows that microörganisms acting in the soil upon added organic materials bring about (*a*) the complete decomposition of much of the organic materials, including most of the carbohydrates and proteins; (*b*) the accumulation of such resistant materials as lignins; (*c*) the reassimilation of part of the carbon and part or all of the nitrogen to form cell protoplasm. The extent to which this latter process goes on depends upon the organisms acting. "If fungi are the active agents of decomposition, one part of nitrogen will be assimilated for every seven or eight parts of carbon given off as CO_2 in the process of energy utilization. If pure cultures of bacteria are the active agents, one part of nitrogen will be assimilated for 12.5 parts of carbon liberated CO_2. Since bacterial cells are richer in nitrogen than are fungus mycelium, a smaller amount of protoplasm will be synthesized. If the mixed soil flora and fauna take part in the decomposition process, one part of nitrogen will be transformed from an inorganic to an organic form for every 16 to 18 parts of carbon given off." This latter process is what ordinarily takes place in the soil. When plant residues or straw is added to the soil in a very short time 60 to 80 per cent of the carbon compounds is decomposed, leaving the remainder in the soil as resistant celluloses, waxes, or lignins. Of this 60 to 80 per cent acted upon, 20 to 70 per cent is given off as CO_2 and 10 to 40 per cent is left in the soil as microbial protoplasm. This indicates that a considerable quantity of the carbon added to a soil in organic materials may be held in the soil as synthesized cell substance. This will contribute to the supply of organic matter or "humus."

The amount of nitrogen utilized by soil microörganisms also varies considerably. In the case of fungi, for every 100 parts of organic matter decomposed, from 0.5 to 4.0 parts of nitrogen will be assimilated. If the organic material contains 0.5 per cent nitrogen, as in the case of straw, additional nitrogen has to be utilized, 1 to 2 parts for every 100 parts of material before complete decomposition takes place. If, however, the added material is clover or alfalfa, containing 1.5 to 2.5 per cent nitrogen, no additional nitrogen is necessary for decay, but no nitrogen will be liberated as NH_3 for a few months. If the proportion of nitrogen runs higher than 2.5 per cent then some of it will at once become available as ammonia.

Bacteria and actinomycetes are not as economical in their utilization of energy materials as fungi, and although their nitrogen content is higher (9 to 13 per cent) the actual amount of nitrogen assimilated is less than in the case of fungi, since they synthesize so much less cell protoplasm. This will result in the liberation of available ammonia from materials having a lower percentage of nitrogen.

In summarizing, the processes carried on by the soil microörganisms result, with materials having a wide carbon-nitrogen ratio, in the use of available soil nitrates, the loss of considerable carbon, and a narrowing of the ratio. If, however, the added substance has a narrow ratio this favors the synthesizing of more cell protoplasm, because of the abundance of nitrogen, with the result that less carbon will be lost, and at the same time nitrogen will be liberated as available nitrates. The result will be a widening of the ratio. A soil having a carbon-nitrogen ratio wider than normal is not in a condition to support plant growth, since the activity of the soil organisms will result in nitrogen starvation. When a soil shows a constant ratio this indicates that there is a proper balance of nitrogen and carbon to meet the needs of the metabolic processes of the soil flora. Some energy material will be utilized and at the same time some nitrogen will be liberated as ammonia. The addition of fresh organic materials having a carbon-nitrogen ratio of 10:1 will result in stimulating the growth of the organisms, the liberation of some CO_2 and the formation of an equivalent amount of ammonia.

EXPERIMENTAL

In none of the investigations cited has there been any work conducted to determine the conditions under which the most organic matter, when introduced in various forms, is retained by the soil. It is evident from the foregoing discussion that the carbon-nitrogen ratio of the materials as well as that of the soil is intimately related to the processes taking place. It was with the purpose of determining the effects of different carbon-nitrogen ratios upon the accumulation of organic matter that these experiments were undertaken.

The soil used was an Ellsworth silt loam, low in carbonates and in organic matter. The original composition was as follows:

Carbon	0.97 per cent
Nitrogen (Kjeldahl)	0.073 per cent
Nitrate nitrogen	6.3 pounds an acre
Phosphorus	0.053 per cent
Potassium	1.40 per cent
pH	4.6
Jones lime requirement	6,270 pounds
Carbon-nitrogen ratio	13.3 to 1

As the pH of the soil was low it was feared that the acidity might inhibit biological activities. Fresh hydrated lime was added at the rate of 4,000 pounds an acre (2,000,000 pounds of soil) at the beginning of the experiment to reduce the acidity to a pH of about 6.0.

As the phosphorus content of this soil was also low it was thought best to prevent its becoming a limiting factor by adding a plentiful supply at the beginning. Superphosphate (20 per cent) was applied at the rate of 1 ton an acre to all cultures with the exception of the blank tests and the soil check.

The suppliers of carbon were employed in such amounts as to add 4,000

pounds of carbon an acre. This was equivalent to adding about 7,000 pounds of humus if the entire amount remained. The organic materials used were corn stover, straw, bluegrass (dry), ragweeds, tobacco stems, wood fiber (sawdust), red clover hay, sweet clover hay, glucose, and cellulose. The composition of these substances is given in table 1. These materials were dried and finely ground to permit a more even distribution in the soil.

The nitrogen supplier used was ammonium nitrate. This was selected because of the belief that it would leave no residue likely to alter the reaction. It was ground fine and added in amounts necessary to adjust the ratios to the desired values.

The ratios selected were 15:1, 10:1, 5:1, and 1:1. It was expected that the 15:1 ratio would be sufficiently wide to promote the loss of considerable carbon and to stimulate some nitrogen fixation. The 10:1 ratio was chosen to typify the normal soil ratio. With this initial ratio it was expected that

TABLE 1

Composition of organic materials used

	CARBON	NITROGEN	C:N RATIO
	per cent	*per cent*	
Corn stover	40.2	0.84	47.8:1
Straw	38.4	0.93	41.3:1
Wood fiber	43.2	0.10	432.0:1
Bluegrass	34.0	1.66	20.5:1
Ragweeds	37.4	3.08	12.0:1
Tobacco stems	34.7	2.02	17.0:1
Red clover	39.7	1.54	26.0:1
Sweet clover	38.6	3.22	12.0:1
Glucose	36.3	0.00	.....
Cellulose	44.0	0.00	.....

the relation of carbon to nitrogen would remain fairly stable with the contribution of a moderate amount of organic matter and the liberating of some available nitrogen. The 5:1 and the 1:1 ratios, being narrow, were expected to cause considerable organic matter to accumulate and also much ammonia or nitrates to be liberated. With this wide variation in ratios a considerable difference in the rates of decomposition was also anticipated.

Some investigators have reported that additions of phosphates to soils in liberal amounts may bring about increased nitrogen fixation. If such were the case the addition of phosphates to the soil should result in less nitrate depression and a larger accumulation of organic matter. To one culture pot for each of the organic materials phosphate only was added at the rate of one ton an acre.

One series of cultures was also included in which all organic materials were incorporated with the limed soil without supplementary additions of ammonium nitrate. These cultures are designated as "blanks."

As a check upon the process taking place in the soil due to liming, four cultures were arranged to which no organic materials were added.

One-half gallon glazed crocks were employed. Each of these was filled with 2.5 pounds of soil to which had been added the proper amounts of organic material and the necessary supply of ammonium nitrate for adjusting the carbon-nitrogen ratio to the desired values. The entire amount of soil used had previously been treated with the hydrated lime and the superphosphate. These culture pots were then brought to optimum moisture content (approximately 24 per cent) with distilled water and kept in a room the temperature

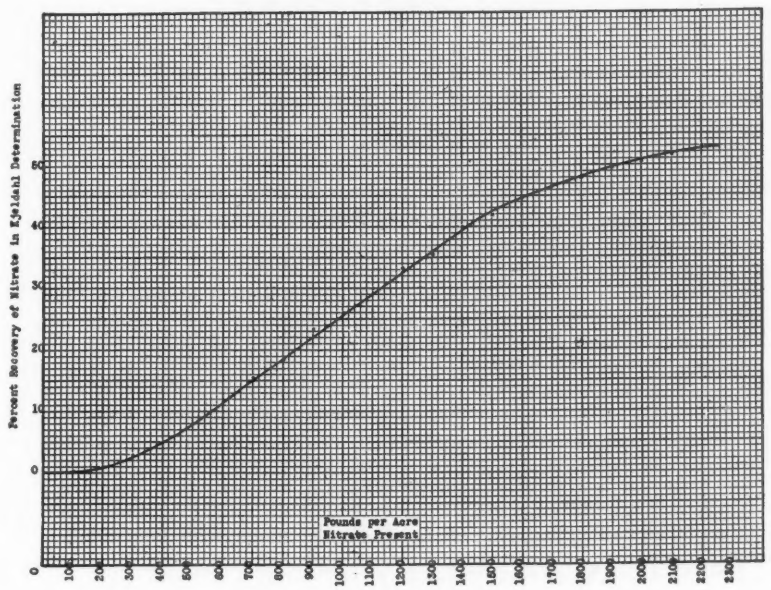


FIG. 1. RELATION OF NITRATE RECOVERY IN THE KJELDAHL METHOD TO THE QUANTITY OF NITRATE PRESENT

and humidity of which was controlled. The temperature was held between 25 and 30°C. The moisture content was adjusted every two weeks, this being frequent enough to limit the loss in water to less than 5 per cent. Samples for analysis were taken at the end of the first, second, fourth, sixth, eighth, and twelfth months. The samples were removed by means of a large cork borer pushed to the bottom of the crocks. The amount removed at each sampling period was about 50 gm. After each sampling the soil was taken out and thoroughly mixed, then replaced. This served to produce good aeration. The samples were dried, ground to pass a 100-mesh screen, and stored in tightly stoppered bottles.

TABLE 2

Organic nitrogen (to each 2,000,000 pounds of soil)

MATERIALS	15:1			10:1			5:1			1:1			PHOSPHATED			BLANKS		
	1st month	6th month	12th month	1st month	6th month	12th month	1st month	6th month	12th month	1st month	6th month	12th month	1st month	6th month	12th month	1st month	6th month	12th month
	pound	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*	*pound*
Corn stover	1,600	1,860	1,850	1,860	1,910	1,890	2,020	1,920	1,885	3,340	3,115	2,580	1,520	1,680	1,430	1,460	1,600	1,300
Straw	.....	.....	.....	1,995	1,800	1,800	2,220	1,855	1,840	3,110	2,910	2,620	1,560	1,620	1,610	1,540	1,620	1,500
Wood fiber	1,620	1,780	1,820	1,790	1,740	1,680	2,115	1,910	1,750	3,110	3,210	3,010	1,600	1,515	1,425	1,480	1,520	1,405
Bluegrass	1,875	1,690	1,780	1,940	1,760	1,860	2,220	1,920	1,890	3,400	3,210	3,080	1,720	1,650	1,540	1,600	1,615	1,555
Ragweeds	.....	.....	.....	1,830	1,880	1,780	2,200	2,040	1,830	3,310	3,300	2,340	1,860	1,860	1,860	1,800	1,855	1,815
Tobacco stems	1,780	1,760	1,780	1,835	1,880	1,815	2,060	1,860	1,860	3,070	2,990	2.930	1,640	1,630	1,600	1,620	1,720	1,675
Red clover	1,660	1,675	1,800	1,780	1,920	1,920	2,060	1,880	1,760	3,460	2,980	2,340	1,660	1,650	1.680	1,620	1,635	1,630
Sweet clover	.....	.....	.....	1,940	1,800	1,800	2,460	2,020	1,850	3,200	3,200	3,230	1,900	1,875	1,720	1,880	1,800	1,800
Glucose	1,755	1,640	1,690	1,785	1,775	1,715	2,020	1,780	1,850	2,980	3,090	2,800	1,440	1,595	1,495	1,420	1,590	1,515
Cellulose	1,760	1,640	1,640	1,740	1,860	1,825	2,135	1,890	1,810	3,040	2,780	2,740	1,520	1,560	1,495	1.480	1,500	1,440
Average	1,720	1,720	1,765	1,850	1,830	1,810	2,150	1,910	1,835	3,200	3,080	2,770	.....	.....	.....	.....	.....	.....
Soil check	1,420	1,480	1,300	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

The results for the 2-, 4-, and 8-month periods are omitted for the purpose of simplification.

TABLE 3

Organic carbon (for pounds to each 2,000,000 pounds of soil multiply results by 1,000)*

MATERIALS	15:1			10:1			5:1			1:1			PHOSPHATED			BLANKS		
	1st month	6th month	12th month	1st month	6th month	12th month	1st month	6th month	12th month	1st month	6th month	12th month	1st month	6th month	12th month	1st month	6th month	12th month
Corn stover	19.91	18.54	18.34	20.86	18.72	18.49	20.67	18.71	18.56	20.75	19.20	18.90	20.59	18.14	18.00	20.67	18.49	17.05
Straw	.....	.....	.....	19.93	19.20	18.54	19.96	18.87	18.63	20.89	19.50	18.73	20.10	18.30	18.35	20.45	18.27	17.37
Wood fiber	20.86	19.09	18.27	20.67	19.22	18.68	20.34	19.36	18.76	20.72	19.41	18.95	20.94	18.50	17.23	21.05	19.80	16.90
Bluegrass	20.78	19.17	18.73	20.86	18.35	18.54	20.20	19.09	18.98	22.09	19.81	19.23	20.86	18.95	17.78	20.45	19.22	18.13
Ragweeds	.....	.....	.....	21.32	18.81	18.27	20.56	19.14	18.54	20.40	19.03	18.65	20.45	18.50	18.00	21.70	19.77	18.73
Tobacco stems	21.13	18.95	18.40	20.61	19.03	18.68	20.86	19.36	18.81	20.72	19.05	18.87	20.20	18.10	17.89	21.54	18.68	18.40
Red clover	20.45	18.32	18.32	20.31	18.84	18.43	19.36	19.00	18.84	20.72	18.46	18.40	19.14	18.19	17.75	19.30	18.40	18.19
Sweet clover	.....	.....	.....	20.45	19.28	18.54	21.00	18.65	18.76	19.50	18.90	18.92	20.12	18.35	18.13	20.89	18.43	18.38
Glucose	19.74	17.48	17.31	20.18	17.37	17.02	19.55	17.72	17.04	19.71	17.67	16.23	18.46	17.15	15.87	18.73	17.45	16.44
Cellulose	18.84	17.40	17.42	18.87	17.89	17.73	19.14	17.72	18.00	19.63	18.43	18.05	20.26	17.18	16.20	21.40	17.50	17.50
Average	20.24	18.42	18.11	20.41	18.67	18.29	20.16	18.76	18.49	20.51	18.95	18.49	.....	.....	.....	.....	.....	.....
Soil check	17.72	16.63	16.36	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

* Carbon reported includes negligible amounts of inorganic carbon.

TABLE 4

Ratios of carbon to nitrogen

MATERIALS	15:1			10:1			5:1			1:1			INITIAL RATIO	PHOSPHATED			BLANKS		
	1st month	6th month	12th month	1st month	6th month	12th month	1st month	6th month	12th month	1st month	6th month	12th month		1st month	6th month	12th month	1st month	6th month	12th month
Corn stover	12.4	9.9	9.8	11.1	9.8	9.8	10.4	9.7	9.9	6.2	6.2	7.3	15.5	13.5	10.8	12.6	14.1	11.5	13.0
Straw	.....	.....	.....	10.0	10.7	10.3	9.0	10.1	9.5	6.7	6.7	7.2	15.0	12.9	11.3	11.4	13.3	11.3	11.5
Wood fiber	12.9	10.7	10.0	11.5	11.0	11.1	9.6	10.1	10.7	6.1	6.1	6.2	16.1	13.1	12.2	12.0	14.2	13.0	12.0
Bluegrass	11.1	11.3	10.5	10.7	10.4	10.0	9.1	9.9	10.0	6.5	6.0	6.2	14.1	12.1	11.5	11.5	12.7	11.9	11.7
Ragweeds	.....	.....	.....	11.6	10.0	10.2	9.3	9.4	10.1	6.2	5.8	8.0	13.1	11.0	10.0	9.7	12.0	10.6	10.3
Tobacco stems	11.8	10.7	10.3	11.2	10.1	10.2	10.1	10.4	10.1	6.9	6.4	6.4	13.8	12.3	11.6	11.2	13.3	10.8	11.6
Red clover	12.3	10.9	10.2	11.4	9.8	9.6	9.4	10.1	10.6	6.0	6.2	8.0	14.5	11.5	11.0	10.5	11.9	11.2	11.2
Sweet clover	.....	.....	.....	10.5	10.7	10.3	8.5	9.2	10.1	6.1	5.9	5.9	13.0	10.6	9.7	10.5	11.1	10.2	10.1
Glucose	11.3	10.6	10.2	11.3	9.8	9.8	9.7	9.9	9.2	6.6	5.7	6.0	16.1	12.8	10.7	10.6	13.2	11.0	10.8
Cellulose	10.7	10.6	10.6	10.8	9.6	9.7	9.0	9.4	9.9	6.4	6.7	6.5	16.1	13.3	10.8	10.8	14.4	11.6	12.1
Average	11.8	10.7	10.2	11.0	10.2	10.1	9.4	9.8	10.0	6.4	6.2	6.8	.....	.....	.....	.....	.....	.....	.....
	Initial ratio	1st month	6th month	12th month															
Soil check	13.3	12.5	11.2	12.5	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

TABLE 5

Nitrate nitrogen (to each 2,000,000 pounds of soil)

MATERIALS	15:1				10:1				5:1				1:1				PHOSPHATED			BLANKS		
	At start	1st month	6th month	12th month	At start	1st month	6th month	12th month	At start	1st month	6th month	12th month	At start	1st month	6th month	12th month	1st month	6th month	12th month	1st month	6th month	12th month
	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.
Corn stover	95	50	120	440	160	110	160	440	360	440	560	520	1,960	1,540	1,920	2,400	50	140	180	40	120	120
Straw	85	...	...	...	150	160	520	560	350	480	640	580	1,950	1,920	1,920	2,160	40	140	200	60	120	80
Wood fiber	135	180	320	320	200	200	520	320	400	360	640	660	2,000	1,920	1,440	1,920	30	160	240	30	120	280
Bluegrass	40	160	440	280	105	320	320	120	305	480	640	480	1,905	1,760	1,760	1,600	60	220	280	60	180	260
Ragweeds	...	...	...	...	35	220	320	360	235	280	520	640	1,835	1,540	1,840	2,560	120	360	320	140	400	320
Tobacco stems	20	100	320	320	85	200	560	400	285	320	720	560	1,885	1,760	1,920	1,760	70	440	320	110	360	400
Red clover	60	50	400	480	125	50	440	440	325	280	640	700	1,925	1,020	1,960	2,240	60	220	320	70	160	240
Sweet clover	...	...	...	...	35	100	480	640	235	480	680	640	1,835	1,720	1,760	1,800	120	360	320	120	320	360
Glucose	135	200	280	320	200	260	400	400	400	280	560	540	2,000	1,760	1,920	2,240	60	220	180	60	240	200
Cellulose	135	280	280	320	200	300	320	240	400	320	520	600	2,000	1,760	1,760	2,400	50	80	200	40	100	240
Average	...	146	308	354	...	192	404	392	...	372	612	592	...	1,670	1,820	2,108	....	....	....	....	....	....
Soil check	...	100	180	100	....	....	....	....	....	....	....	....	.....	.....	.....	.....	....	....	....	....	....	....

Nitrogen was determined by the Kjeldahl method and nitrate nitrogen was measured by the phenoldisulfonic acid method. In order to determine the extent to which nitrate nitrogen was included in the Kjeldahl determination a considerable number of total nitrogen determinations were made by a modification of the Davisson method.[3] This method requires so much time that it does not lend itself to large numbers of determinations. It was found, however, that the fractional recovery of nitrate nitrogen in the standard Kjeldahl method was a function of the total amount of nitrates present and that by the application of a correction factor, total nitrogen including nitrates

TABLE 6

Gain or loss in total nitrogen at end of twelfth month (by each 2,000,000 pounds of soil)

MATERIALS	15:1	10:1	5:1	1:1	PHOSPHATED	BLANKS
	pounds	*pounds*	*ponnds*	*pounds*	*pounds*	*pounds*
Corn stover	+560	+470	+145	−480	+110	−120
Straw	.....	+500	+160	−580	+250	+20
Wood fiber	+410	+140	+150	−530	+205	+225
Bluegrass	+330	+120	+110	−780	+165	+160
Ragweeds	.....	+280	+210	−560	+390	+345
Tobacco stems	+370	+350	+160	−770	+230	+385
Red clover	+550	+500	+200	−880	+390	+260
Sweet clover	.....	+580	+230	−430	+250	+370
Glucose	+280	+250	+130	−420	+215	+255
Cellulose	+230	+200	+150	−320	+235	+220
Average	+390	+339	+165	−575	.....	.....

could be estimated with fair accuracy from the results of the Kjeldahl determination.

Table 2 shows the corrected amounts of organic nitrogen[4] to the acre.

The electric combustion method was employed for determining organic carbon (table 3)

The ratios of carbon to nitrogen, calculated from the foregoing carbon and nitrogen values, are presented in table 4.

The quantities of nitrate nitrogen found at successive periods are presented in table 5.

By calculating the total amount of nitrogen present in the soil, the organic

[3] The original Davisson method consists in reducing the nitrates with Devarda's alloy under slightly alkaline conditions. It employs 0.1 *N*/NaOH solution and boiling for 20 minutes. This did not give complete recovery with known solutions, therefore 0.25 *N*/NaOH solution was substituted and the mixture permitted to stand in the cold over night. After acidifying with 35 cc. of H_2SO_4 and evaporating off the water the regular Kjeldahl procedure was followed. The graph constructed from the results of these determinations and used to facilitate the calculations of the amounts of organic nitrogen is given as figure 1.

[4] Organic nitrogen includes any ammonia nitrogen remaining unnitrified from that originally supplied as ammonium nitrate.

nitrogen plus the nitrate nitrogen, and from this subtracting the nitrogen present at the beginning of the year, that nitrogen added by fixation or lost by denitrification can be obtained for any period. The results for the12-month period are shown in table 6.

DISCUSSION

The principal purpose of this investigation was to determine the influence of the carbon-nitrogen ratio of organic additions upon the accumulation of organic matter in the soil, as estimated from organic carbon. The amounts of carbon (table 3) show that regardless of the sources of the carbon the quantities present at the end of the year fall within a rather narrow range. It is perhaps to be expected that different materials adjusted to a common ratio would show little variation except possibly in the rapidity of change. Such seems to be the case.

The 15:1 ratio has resulted in the accumulation of least carbon as measured after 12 months incubation. Such a ratio evidently encourages the evolution of much carbon as carbon dioxide, the energy material being in excess of the supply of available nitrogen. For each material the amount of carbon remaining is less than with the narrower ratios. Thus it appears that a wide ratio is not conducive to the best accumulation of organic matter. With this wide ratio there should be a tendency for nitrogen fixation to occur. Krishna (17) has recently shown that straw and other carbonaceous materials can furnish energy for nitrogen fixation. Table 6 shows that fixation has occurred with all materials, although to the greatest extent with the more carbonaceous. With corn stover, wood fiber, and red clover the organic nitrogen content increased from approximately 1,600 to over 1,800 pounds an acre by the end of the year. When soils are treated with wide ratio materials there is a tendency for the ratio to become narrower as a result of the loss of carbon and the fixation of nitrogen. This is indicated in table 4. From an initial ratio of 15 to 1, soils treated with corn stover narrowed to 9.8 to 1, and those treated with red clover to 10.2 to 1. Other treatments showed similar results.

The 10 to 1 ratio was thought to represent the stable relation for soils of the region. That such is the case is shown by the amounts of organic carbon and nitrogen remaining in the soils for those cultures having this initial ratio. While there was an evolution of some carbon as carbon dioxide there was an equivalent release of nitrogen as nitrates or otherwise. This resulted in the ratio of carbon to nitrogen remaining practically stable. Table 4 indicates that at the beginning of the year nitrogen was lost more rapidly than organic carbon, resulting in a widening of the ratios. But, after a short time the carbon losses were sufficiently large so that the ratio remained approximately 10 to 1.

The 5:1 and 1:1 ratios have resulted in the largest storage of organic carbon (table 3). This is in accord with the expectation that a narrow ratio should encourage the holding of carbon and the release of nitrogen.

Figure 2 shows the trend of the various ratios plotted from the averages. It indicates the tendency to stabilize at the 10 to 1 ratio. That a narrow ratio of carbon to nitrogen favors the loss of nitrogen is shown in table 6. From the amounts of organic nitrogen in the materials it is seen (table 2) that a considerable loss occurred in every case with the narrow ratios. The rate of loss of nitrogen was much greater than the decrease in organic carbon, this causing a widening of the carbon-nitrogen ratio, as shown in table 4. The 5 to 1 ratios have widened in all cases, the final results ranging from 9.2 to 10.7:1. The 1 to 1 ratio has also spread considerably, ending at values ranging from 6.0 to 8.0:1.

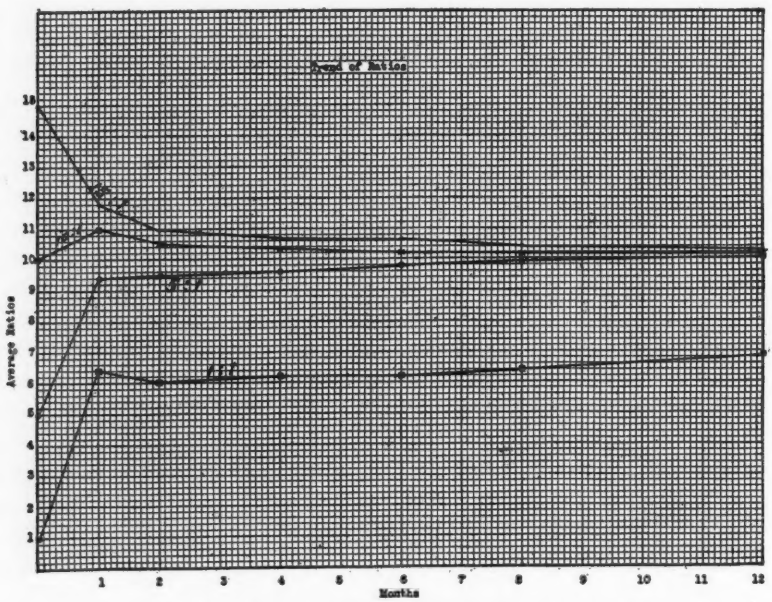


FIG. 2. TREND OF CARBON TO NITROGEN RATIOS

The availability of the nitrogen as measured by the nitrate production varied greatly with the different ratios (table 5). From the analyses reported it is apparent that the 15:1 ratio at no time furnished much available nitrogen. During the first months several of the organic materials, (Blanks), corn stover, tobacco stems, and red clover caused a marked nitrate reduction. The 10 to 1 ratio cultures show a larger production of nitrates. This is probably because the supply of nitrogen meets the needs of the microörganisms and nitrogen is liberated in proportion as carbon is utilized as a source of energy. The largest amounts of nitrates present are found with the 5 to 1 and the 1 to 1 ratios. The quantities amount to as much as 2,500 pounds an acre. These results are in

accord with the findings of Waksman (31) and of Lyon, Bizzell, and Wilson (18). They indicate that with nitrogen in excess of the energy supply nitrogenous materials will be utilized as a source of energy and nitrogen will be liberated as ammonia, later being nitrified to nitrates.

Waksman and Tenney (34), Whiting (36), and others have shown that the rate of decomposition of organic materials varies directly with the amounts of soluble constituents and of available nitrogen. Those materials having the larger amounts of these components will undergo decay most rapidly. Tables 2 and 3 show that there is a difference in the rates at which these organic materials have undergone decay. During the first month the most rapid action took place with the wide-ratio materials. Waksman points out that, with readily available nitrogen supplied, many highly carbonaceous materials will decay very rapidly because of their high content of cold-water soluble constituents. This probably was the case with these organic substances. By the end of the second month, however, the most readily available components

TABLE 7

Order of rapidity of decomposition (most rapid at top)

FIRST MONTH	SECOND MONTH	FOURTH MONTH	SIXTH MONTH	EIGHTH MONTH	TWELFTH MONTH
Straw	Ragweeds	Sweet clover	Sweet clover	Sweet clover	Sweet clover
Corn stover	Sweet clover	Red clover	Red clover	Red clover	Ragweeds
Red clover	Red clover	Corn stover	Corn stover	Ragweeds	Red clover
Bluegrass	Corn stover	Ragweeds	Ragweeds	Corn stover	Straw
Wood fiber	Straw	Bluegrass	Tobacco stem	Wood fiber	Corn stover
Tobacco stem	Wood fiber	Straw	Blue grass	Straw	Wood fiber
Sweet clover	Bluegrass	Wood fiber	Straw	Tobacco stem	Tobacco stem
Ragweeds	Tobacco stem	Tobacco stem	Wood fiber	Bluegrass	Bluegrass

of these wide-ratio materials probably were largely decomposed, since from this time on, the narrow ratio materials showed the most rapid rate of change. The order of the rates of decomposition, as determined from the data for organic carbon and organic nitrogen, considering the losses in each interval of time, is given in table 7.

The results obtained with the blank cultures (table 8) show that at the end of the year the amounts of organic carbon remaining in the soil are directly in accord with the carbon-nitrogen ratios. Ragweeds, sweet clover, and tobacco stems, those materials having the narrower ratios, have resulted in the accumulation of most organic matter. The artificial materials, glucose and cellulose, have shown large losses of carbon. These results support the statement of Russell (23) that to increase carbon in a soil it is necessary also to increase the nitrogen supply. Wide-ratio materials containing little nitrogen do not favor carbon accumulation.

The depression of nitrates characteristic of applications of straw and other wide-ratio materials is noticeable in the blank test cultures (table 5). In the

check soil the quantity of nitrate nitrogen at the end of the first month was 100 pounds an acre. This increased slightly during the year. When wood fiber, straw, bluegrass, corn stover, and other materials low in nitrogen were added to the soil the quantity of nitrate nitrogen was reduced to 30 to 40 pounds an acre, indicating considerable nitrate consumption. In some cases the depression of the nitrates was manifest during most of the 12-month period. The only materials which did not reduce nitrate nitrogen were those having a carbon-nitrogen ratio lower than 20:1.

Nitrogen fixation is also observed to have taken place with the blank tests. Table 6 shows that at the end of the year some fixation had occurred in all cases except with applications of straw and corn stover. The largest amount

TABLE 8

Summary of blank cultures.

MATERIAL	INITIAL RATIO	ORGANIC CARBON*				ORGANIC NITROGEN			
		Original	12th month	Loss	Gain over check	Original	12th month	Gain or loss	Gain over check
		pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
Corn stover	15.5:1	23.40	17.05	6.35	0.69	1,540	1,300	−240	0
Straw	15.0:1	23.40	17.37	6.03	1.01	1,560	1,500	−60	200
Wood fiber	16.1:1	23.40	16.90	6.50	0.54	1,460	1,405	−55	105
Bluegrass	14.1:1	23.40	18.13	5.27	1.77	1,650	1,555	−90	255
Ragweeds	13.1:1	23.40	18.73	4.67	2.37	1,790	1,815	+25	515
Tobacco stems	13.8:1	23.40	18.40	5.00	2.04	1,690	1,675	−15	375
Red clover	14.5:1	23.40	18.19	5.21	1.83	1,610	1,630	+20	330
Sweet clover	13.0:1	23.40	18.38	5.02	2.02	1,790	1,800	+10	500
Glucose	16.1:1	23.40	16.44	6.96	0.08	1,460	1,515	+55	215
Cellulose	16.1:1	23.40	17.50	5.90	1.14	1,460	1,440	−20	140
Soil check	13.3:1	19.40	16.36	3.04	....	1,460	1,300	−160	...

* Multiply by 1,000 for 2,000,000 pounds soil.

of nitrogen fixed was found with the addition of narrow-ratio materials. This would seem to indicate that nitrogen-fixing organisms are benefitted by the presence of some nitrogen in their energy material. This may be an indirect benefit, however, as other microörganisms would bring about a more rapid decomposition of such materials and this might render the nitrogen more available for nitrogen fixers.

As previously indicated one series of cultures was prepared with the view of determining the degree to which the addition of superphosphate stimulated nitrogen fixation. By comparing the amounts of nitrogen fixed (table 6) by the phosphate cultures with those of the blanks it will be noted that there is no consistent indication that phosphates have had this effect.

CONCLUSIONS

The results obtained with the Ellsworth silt loam soil employed in these experiments and under the conditions set up lead to the following conclusions:

With a given carbon-nitrogen ratio the microörganic processes taking place in the soil are similar, regardless of the organic materials added.

A ratio wider than 10 to 1 causes the loss of organic carbon from the soil.

A ratio narrower than 10 to 1 leads to the saving of organic carbon.

A wide ratio causes nitrate depression over several months whereas a narrow ratio leads to the formation of nitrates.

Wide-ratio materials may be sources of energy for nitrogen fixation, but this nitrogen will not be available to crops until losses of carbon have narrowed the carbon-nitrogen ratio to about 10:1.

Applications of phosphates do not cause appreciably greater nitrogen fixation.

Sufficient nitrogen to narrow the ratio to about 15:1 favors nitrogen fixation.

REFERENCES

(1) ALBRECHT, W. A. 1922 Nitrate accumulation under straw mulch. *Soil Sci.* 20: 253–265.

(2) ALWAY, F. J., AND MCDOLE, G. R. 1916 The loess soils of the Nebraska portion of the transition region: I. Hygroscopicity, nitrogen, and organic carbon. *Soil Sci.* 1: 192–238.

(3) ALWAY, F. J., AND TRUMBULL, R. S. 1910 A contribution to our knowledge of the nitrogen problem under farming. Jour. Indus. and Engin. Chem. 2: 135–138.

(4) ALWAY, F. J., AND VAIL, C. E. 1912 The relative amounts of nitrogen, carbon, and humus in some Nebraska soils. *Nebr. Agr. Exp. Sta. 25th Ann. Rept.* 1912: 145–163.

(5) AMES, J. W., AND GAITHER, E. W. 1913 Composition of calcareous and non-calcareous soils. Ohio Agric. Exp. Sta. Bul. 261.

(6) ANDERSON, J. W. 1926 The influence of available nitrogen on the fermentation of cellulose in the soil. *Soil Sci.* 21: 115–126.

(7) BARTHEL, CHR., AND BENGTSSON, N. 1924 Action of stable manure in the decomposition of cellulose in tilled soil. *Soil Sci.* 18: 185–200.

(8) BLAIR, A. W., AND MCLEAN, H. C. 1917 Total nitrogen and carbon in cultivated land, and land abandoned to grass and weeds. *Soil Sci.* 4: 283–293.

(9) BLAIR, A. W., AND PRINCE, A. L. 1928 The influence of heavy applications of dry organic matter on crop yields and on nitrate content of the soil. *Soil Sci.* 25: 281–289.

(10) BROWN, P. E., AND ALLISON, F. E. 1916 The influence of some common humus-forming materials of narrow and wide nitrogen-carbon ratios on bacterial activities. *Soil Sci.* 1: 49–75.

(11) BROWN, P. E., AND O'NEAL, A. M. 1923 The color of soils in relation to organic matter content. Iowa Agr. Exp. Sta. Res. Bul. 75.

(12) COLLISON, R. C., AND CONN, H. J. 1925 The effect of straw on plant growth. N. Y. Agr. Sta. Tech. Bul. 114.

(13) DORYLAND, C. J. T. 1916 The influence of energy material upon the relation of soil microörganisms to soluble plant food. N. Dak. Agr. Exp. Sta. Bul. 116.

(14) DYER, B. 1902 Results of investigations of Rothamsted soils. U. S. Dept. Agr. Bul. 106.

(15) HUTCHINSON, H. B. 1919 The influence of sugar and plant residues on losses of soil nitrates. *Jour. Agr. Sci.* 9: 107.

(16) JENNY, HANS 1928 Relation of climatic factors to the amount of nitrogen in soils. *Jour. Amer. Soc. Agron.* 20: 900–913.

(17) KRISHNA, P. G. 1928 Cellulose decomposition products as sources of energy for azotobacter and B. Amylobacter. *Jour. Amer. Soc. Agron.* 20: 511–515.

(18) LYON, T. L., BIZZELL, J. H., AND WILSON, B. D. 1923 Depressive influence of certain higher plants on the accumulation of nitrates in the soil. *Jour. Amer. Soc. Agron.* 15: 457–466.

(19) MARTIN, T. L. 1925 Effect of straw on accumulation of nitrates and crop growth. *Soil Sci.* 20: 159–164.

(20) MERKLE, F. G. 1918 The decomposition of organic matter in soils. *Jour. Amer. Soc. Agron.* 10: 281–302.

(21) MURRAY, T. J. 1921 The effect of straw on biological soil processes. *Soil Sci.* 12: 233–259.

(22) READ, J. W. 1921 Practical significance of the organic carbon-nitrogen ratios in soils. *Soil Sci.* 12: 491–495.

(23) RUSSELL, E. J. 1927 Soil Conditions and Plant Growth. Longmans, Green and Co., New York.

(24) SCOTT, H. 1921 The influence of wheat straw on the accumulation of nitrates in the soil. *Jour. Amer. Soc. Agron.* 13: 233–258.

(25) SIEVERS, F. J., AND HOLTZ, H. F. 1926 The significance of nitrogen in soil organic matter relationships. Wash. Agr. Exp. Sta. Bul. 206.

(26) STARKEY, R. L. 1924 Some observations on the decomposition of organic matter in soils. *Soil Sci.* 17: 293–315.

(27) STEWART, R. 1910 Quantitative relationships of carbon, phosphorus, and nitrogen in soils. Ill. Agr. Exp. Sta. Bul. 145.

(28) THOMAS, R. P., AND HARPER, H. J. 1926 The use of oat straw in a system of soil fertility. *Soil Sci.* 21: 393–400.

(29) WAKSMAN, S. A. 1924 Influence of microörganisms upon the carbon-nitrogen ratio in soils. *Jour. Agr. Sci.* 14: 555–562.

(30) WAKSMAN, S. A. 1926 The rôle of microörganisms in the formation of "humus" in the soil. *Soil Sci.* 22: 421–436.

(31) WAKSMAN, S. A. 1927 Principles of Soil Microbiology. Williams and Wilkins, Baltimore, Md.

(32) WAKSMAN, S. A. 1929 Chemical and microbiological principles underlying the decomposition of green manures in the soil. *Jour. Amer. Soc. Agron.* 21: 1–18.

(33) WAKSMAN, S. A., AND STARKEY, R. L. 1924 Influence of organic matter upon the development of fungi, actinomycetes, and bacteria in the soil. *Soil Sci.* 17: 373–377.

(34) WAKSMAN, S. A., AND TENNEY, F. G. 1928 Composition of natural organic materials and their decomposition in the soil: III. The influence of nature of plant upon the rapidity of its decomposition. *Soil Sci.* 26: 156–171.

(35) WAYNICK, D. D., AND SHARP, L. T. 1919 Variations in nitrogen and carbon in field soils and their relation to the accuracy of field trials. *Univ. Cal. Pub. Agr. Sci.* 4: 121–139.

(36) WHITING, A. L. 1926 Some important factors controlling the rate of nitrification of organic materials. *Jour. Amer. Soc. Agron.* 18: 854–875.

(37) WHITING, A. L., AND SCHOONOVER, W. R. 1920 The comparative rate of decomposition of green and cured clover tops in soil. *Soil Sci.* 9: 137–149.

(38) WILSON, B. D., AND WILSON, J. K. 1925 An explanation for the relative effects of timothy and clover residues in the soil on nitrate depression. N. Y. (Cornell) Agr. Exp. Sta. Mem. 95.

PHOSPHORUS ASSIMILATION BY SOIL MICROÖRGANISMS

L. G. THOMPSON, JR., F. B. SMITH AND P. E. BROWN

Iowa State College

Received for publication August 18, 1930

It is well known that microörganisms in their metabolism absorb certain soluble inorganic soil constituents. This is especially true of phosphorus, which is found in considerable amounts in microbial protoplasm. This phosphorus, on the death and decomposition of the organisms, may again be made available for plant-food.

Many microörganisms, when growing under favorable conditions, have been found to liberate carbon dioxide and bring about a change in the composition of the medium upon which they are growing. Water charged with carbon dioxide will attack many relatively insoluble soil constituents, among which is tri-calcium phosphate, from which soluble phosphates are formed. Then, too, the microörganisms, among other products of growth, may form various organic acids, which, when they come in contact with the insoluble tri-calcium phosphate, will bring the phosphorus into solution. In this connection it may be noted that there is a possibility that the phosphorus in the bodies of the dead organisms may become available through the action of autolytic enzymes without the intervention of microörganisms.

Whether these reactions will lead to an increase in the water-soluble phosphorus in the soil will depend upon whether or not the analytical processes are proceeding more rapidly than the synthetic reactions. There is also the possibility that the organic phosphorus which is soluble in pure water may be more available to the plant than is the inorganic phosphorus from which it was produced through the activity of the soil microörganisms.

In a study of cultures of 20 soil molds, Brown and Smith (1) found that *Tetracoccosporium paxianum* in solution cultures gave an increase in water-soluble phosphorus, all the others showing a decrease or a phosphate assimilation. No definite relationship between phosphate-assimilating power and change of reaction in culture solutions was shown.

The purpose of this work was to study further the assimilation of phosphorus by soil microörganisms, the utilization of various carbon compounds, acid production and its effect upon the water-soluble phosphorus of the soil.

EXPERIMENTAL

Phosphorus assimilation by molds in dextrose solution cultures

Two hundred cubic centimeters of a sterile culture medium containing 3 per cent dextrose, 0.05 per cent mono-potassium phosphate, 0.2 per cent sodium

nitrate, 0.1 per cent potassium chloride, 0.05 per cent magnesium sulfate, and 0.01 per cent ferrous sulfate in 500-cc. Erlenmeyer flasks were inoculated in triplicate with pure cultures of *Aspergillus minutus*, *Aspergillus luchuensis*, and *Aspergillus terreus*. The cultures were incubated at 25°C. for 16 days. After incubation, the reaction of the culture medium and the percentage of dextrose remaining were determined. The mycelium was removed, weighed, and the total phosphorus content determined. The acidity of the culture solution was also determined. The quinhydrone electrode was used to determine the pH, and the acidity was measured by titrating an aliquot of the medium against standard alkali. The dextrose was determined by the modified method of Shaffer and Hartmann (2). The phosphorus in the mycelium was brought

TABLE 1

Phosphorus assimilation by molds in dextrose solution cultures

ORGANISM	REACTION OF CULTURE	ACIDITY AS FORMIC ACID	WEIGHT OF MYCELIUM AFTER 2 WEEKS	PO_4 IN MYCELIUM	PO_4 ASSIMILATED	DEXTROSE IN MEDIUM
	pH	*per cent*	*gm.*	*per cent*	*mgm.*	*per cent*
Aspergillus minutus	6.76	....	1.2733	0.54	6.88	.....
Aspergillus luchuensis	2.57	9.20	1.4486	0.33	4.78	0.019
Aspergillus terreus	5.64	1.43	1.4380	0.33	4.75	0.085
Control	5.40	....	.....	....	....	3.000

TABLE 2

Phosphorus assimilation by Aspergillus luchuensis in sucrose solution cultures

LENGTH OF INCUBATION	REACTION OF CULTURE	ACIDITY AS FORMIC ACID	WEIGHT OF MYCELIUM	PO_4 IN MYCELIUM	PO_4 ASSIMILATED
days	*pH*	*per cent*	*gm.*	*per cent*	*mgm.*
11	3.27	0.112	1.5800	....	.....
16	3.70	.....	1.3646	0.78	10.63
21	4.33	0.038	1.2835	....	.....
Control	5.63	0.009	.....	....	.....

into solution with concentrated nitric acid and determined colorimetrically by the method of Parker and Fudge (3). The results of this experiment are given in table 1.

Phosphorus assimilation by Aspergillus luchuensis *in sucrose and dextrin solution cultures*

In the aforementioned experiment *Aspergillus luchuensis* produced a considerable acidity in the dextrose medium. This organism was selected for a further study of its growth, phosphate assimilation, and acid production using sucrose and dextrin as sources of carbon. Cultures were inoculated into a liquid medium similar to the one used in the preceding experiment, except that

3 per cent of sucrose was used instead of dextrose. Duplicate cultures were examined after 11, 16, and 21 days. In addition to the tests made in the preceding experiment, qualitative tests for various organic compounds were made. These tests showed the presence of formic, acetic, and succinic acids. No alcohols, aldehydes, nor acetones were found. The results are presented in table 2.

Qualitative tests showed an almost complete disappearance of sucrose after 21 days. No doubt some of the acids were neutralized by the sodium and potassium liberated by the utilization of nitrate and a larger phosphate assimilation. Then, too, there is the possibility that the organism decomposed the acids further. The mycelium contained 0.78 per cent phosphate at this time, 10.73 mgm. of phosphate being assimilated. The phosphorus in the mycelium was not determined after 11 and 21 days incubation. Apparently sucrose was more readily utilized than dextrose by *Aspergillus luchuensis*. The weight of mycelium produced by *Aspergillus luchuensis* in sucrose solution decreased with increasing incubation period. This was probably due to a solution of the

TABLE 3

Phosphorus assimilation by Aspergillus luchuensis in dextrin solution cultures

LENGTH OF INCUBATION	REACTION OF CULTURE	ACIDITY AS FORMIC ACID	WEIGHT OF MYCELIUM	PO_4 IN MYCELIUM	PO_4 ASSIMILATED
days	*pH*	*per cent*	*gm.*	*per cent*	*mgm.*
22	4.85	0.046	1.0685	Trace	.....
32	....	0.055	1.1270	0.03	0.3381
38	4.92	0.046	1.0560	0.09	0.9504
Control	5.43	.....	.....	....	.....

mycelium, since the energy material had been quickly utilized and the organism could make no further growth.

Growth of this organism was very slow in a dextrin solution medium similar to the sucrose medium, except that dextrin was used to supply carbon and a part of the phosphate was supplied as di-ammonium phosphate and a part as mono-potassium phosphate (table 3). The acidity of the medium was increased but slightly and the percentage of titrable acidity was low, probably because of the liberation of some ammonia from the ammonium phosphate. The amount of mycelium produced in 22 days in dextrin solution medium was but slightly less than the amount produced in dextrose or sucrose in 16 days but the phosphorus content of the mycelium was low and only 0.9504 mgm. of phosphate were assimilated after 38 days.

Phosphorus assimilation by Azotobacter chroococcum *in soil cultures*

Another experiment was planned to determine the effect of a pure culture of *Azotobacter chroococcum* upon the water-soluble phosphorus of the soil, and also upon chemically pure tri-calcium phosphate when added to the soil. The

effect of the native soil flora upon the solubility of tri-calcium phosphate was also determined.

One hundred grams of Carrington loam were placed in each of 54 500-cc. Erlenmeyer flasks. There were two series as follows:

Flask No.	*Series A sterile*
1, 2, 3	Check
4, 5, 6	Inoculated with *Az. chroococcum*
7, 8, 9	1 gm. of tri-calcium phosphate added
10, 11, 12	1 gm. of tri-calcium phosphate added and inoculated with *Az. chroococcum*
	Series B not sterile
13, 14, 15	Check
16, 17, 18	1 gm. of tri-calcium phosphate added

One-half gram of dextrose was added to each flask. The moisture content of the soil was adjusted to 50 per cent of the saturation capacity by the addition

TABLE 4

Phosphorus assimilation in Carrington loam by Azotobacter chroococcum

TREATMENT	WATER-SOLUBLE PHOSPHORUS					
	After 21 days	Assimilated in 21 days	After 45 days	Assimilated in 45 days	After 90 days	Assimilated in 90 days
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Sterile check	3.8	...	3.6	...	3.8	.....
Sterilized and inoculated with *A. chroococcum*	1.4	2.4	0.6	3.0	4.6	−0.8
Sterilized and 1 gm. $Ca_3(PO_4)_2$ added	31.3	...	31.0	...	28.6	.....
Sterilized, 1 gm. $Ca_3(PO_4)_2$ added and inoculated with *A. chroococcum*	28.0	3.3	25.6	5.4	34.2	−5.6
Unsterile check	Trace	...	0.2	...	0.8	.....
Unsterilized and 1 gm. $Ca_3(PO_4)_2$ added	43.6	...	40.6	...	61.2	.....

of sterile, distilled water. Three sets of 18 flasks each were made up; one set was incubated for 21 days, the second set for 45 days, and the third set for 90 days. At the end of each incubation period the water-soluble phosphorus was determined by the colorimetric method of Parker and Fudge (3).

Table 4 gives the amount of water-soluble phosphorus in parts per million for the various treatments and the different incubation periods, and the phosphate assimilated. For the first 21 days there was a decrease of 2.4 milligrams and for 45 days, 3.0 milligrams in water-soluble phosphorus in the sterile soils inoculated with *Azotobacter chroococcum* as compared to the sterile check soils. This was found to be true in both the untreated soils and in the soils treated with tri-calcium phosphate, the decrease being larger in the phosphate-treated soils. This indicates that under the conditions of the experiment, *Azotobacter chroococcum* assimilated more phosphorus than was made available by their

analytic processes. During the next 45 days there was an increase in water-soluble phosphorus in the inoculated soils. This was probably due to the death and decomposition of the Azotobacter cells through the action of autolytic enzymes, thus liberating water-soluble phosphorus.

When the sterile check soil to which tri-calcium phosphate was added, is compared with the unsterile soil receiving the same treatment, it is apparent that the natural soil flora increased the amount of water-soluble phosphorus for the first 21 days. This indicates that the soluble phosphorus formed by the analytic reactions exceeded the phosphorus absorbed by the synthetic reactions. During the next 24 days there was a slight decrease in water-soluble phosphorus, which was probably due to the more rapid growth of certain species or the dying out of certain other species thus changing the ratio between the analytic and the synthetic reactions. For the next 45 days there was a large increase in water-soluble phosphorus in the unsterile soil, which may be due partly to the death and decomposition of the phosphate-assimilating bacteria and partly to a shift in species relationships in the soil.

In the case of the unsterile soil, to which no tri-calcium phosphate was added the quantity of water-soluble phosphorus increased during the course of the experiment, showing that the natural soil flora of this soil at least, assimilated less phosphorus than was made available by their analytic processes.

SUMMARY AND CONCLUSIONS

Aspergillus luchuensis increased the hydrogen-ion concentration of liquid culture media considerably in 11 days to two weeks but the reaction became less acid as the incubation period was increased. *Aspergillus minutus* decreased the hydrogen-ion concentration in dextrose solution cultures after two weeks. This organism did not produce as much mycelium as *Aspergillus luchuensis* but it contained a larger percentage of phosphorus and assimilated more phosphate. If the assimilation of phosphorus is accompanied by a decrease in the hydrogen-ion concentration of the culture medium, *Aspergillus minutus* may have produced more acidity than *Aspergillus luchuensis*, the acidity being neutralized earlier in the incubation period. The phosphorus assimilation by *Aspergillus luchuensis* was small in dextrin and sucrose solution cultures. *Azotobacter chroococcum* assimilated more phosphorus for the first 45 days than was made available, but for the second period of 45 days more phosphorus was made available than was utilized. The addition of insoluble phosphate increased the amount of phosphorus assimilated during the first 45 days of the experiment and also increased the amount of water-soluble phosphorus during the second 45 days. The native soil flora of Carrington loam was more effective in dissolving tri-calcium phosphate than was *Azotobacter chroococcum*. Different species of soil microörganisms probably affect the water-soluble phosphorus differently, for some species may have a greater dissolving action than assimilating power, whereas with other species the reverse may be the case.

REFERENCES

(1) BROWN, P. E., AND SMITH, F. B. 1930 Phosphorus assimilation by certain soil molds. *Iowa State Col. Jour. Sci.* 3: 325.

(2) FRED, E. B., AND WAKSMAN, S. A. 1928 Laboratory Manual of General Microbiology, 72. McGraw-Hill Book Company, Inc., New York.

(3) PARKER, F. W., AND FUDGE, J. F. 1927 Soil phosphorus studies: I. The colorimetric determination of phosphorus in soil extracts and soil solutions. *Soil Sci.* 24: 109.

CHEMICAL METHODS FOR ESTIMATING THE AVAILABILITY OF SOIL PHOSPHATE

P. L. HIBBARD

University of California[1]

Received for publication August 13, 1930

The purpose of this paper is to record the main points of interest developed by the writer during the past three years of an investigation of chemical methods for determining the availability to plants of soil phosphate. Since the days of Liebig this has been a live question, and it still lacks a satisfactory answer.

Available soil phosphate is, for the present purpose, defined as "that part of the soil phosphate which may be absorbed or used by ordinary crop plants in the production of plant substances." Also it is assumed that different species of plants may have quite unlike power to obtain an adequate supply of phosphate from a given soil which is deficient in available phosphate.

In the endeavor to find a somewhat satisfactory procedure, several methods proposed by others have been examined (the results are reported at the end of this paper), much experimental work has been done, and some new methods have been worked out. It is thought that some of the new methods permit a closer approach to an adequate solution of the problem than any previously published chemical methods.

INTRODUCTION

A satisfactory estimation of the availability of soil phosphate by chemical methods may be difficult or impossible for several reasons. Some are here mentioned.

Phosphorus occurs in the soil in several forms of combination, both mineral and organic. This paper is concerned with mineral phosphate only. Apatite, $Ca_3(PO_4)_2CaF_2$; chlorapatite, $Ca_3(PO_4)_2CaCl_2$; hydroxyapatite, $(Ca_3(PO_4)_2)_3Ca(OH)_2$; wagnerite, magnesium phosphate; and wavellite, aluminum phosphate, are soil minerals. According to Russell (21), hydroxyapatite is probably the chief source of soil phosphate. These minerals are relatively insoluble in water. Since most mineral phosphates are very insoluble in water, there is but little PO_4 dissolved in the soil solution at any one time. The amount of PO_4 in solution is increased by CO_2 or other acids, provided they do not at the same time increase too much the concentration of those cations which tend so repress the dissolving of phosphate.

[1] Division of Plant Nutrition.

Some students believe that plants have power to absorb certain nutrients from the solid state, without first having to be dissolved in the soil solution. This is said to be true of phosphates. Also plants have the power of selection so that they can take up PO_4 without at the same time absorbing the cations combined with it.

Another difficulty in estimating the availability to plants of soil phosphate by chemical means is found in the fixation of PO_4 by the soil so that it becomes insoluble in the soil solution and largely unavailable to plants. The determination of whether fixation is a purely chemical phenomenon or is more or less dependent on surface action and colloidal effects has not been made a part of this study. It seems probable that the availability of fixed phosphate depends much on the form in which it is fixed, particularly as to whether it is combined with Fe, Al, or Ca, but chemical agents do not well separate these different phosphates.

Even though the supply of available phosphate is adequate, plants may fail on account of the lack of some other nutrient or perhaps from the presence of some unknown or unsuspected injurious or toxic substance or condition, but such adversities to plants will have little effect on the solubility of soil phosphate in chemical reagents. Since chemical methods of estimating the availability of phosphate depend on first getting it into solution, and since chemical solubility may be very little dependent on several of the aforementioned factors, it is evident that chemical methods can not well be expected to imitate the action of plants in estimating the availability to plants of soil phosphate.

After plants have grown upon a soil which has been treated with phosphate, it seems unreasonable to expect that any chemical test applied to the cropped soil will give a proper representation of the soil as the plant had to deal with it at the start immediately after the phosphate was added, particularly if the phosphate was mostly water-soluble at first.

EXPERIMENTAL

To enable the reader to understand better the experimental work recorded in the following, there is presented on page 439 a tabular statement giving the laboratory number, name, response to phosphate fertilizers, and general fertility of the soils most used in this work.

The methods used in obtaining soil extracts for this study are of two kinds: equilibrium methods, in which the soil is shaken with a volume of solution for some time, then the filtered solution is analysed; and percolation methods, by which the soil is percolated with a solvent to more or less complete removal of PO_4 or other ions, then the percolate is examined. The numerical results obtained by these two procedures are usually unlike and not properly comparable. It is not intended to convey the idea that complete equilibrium is attained in the first case, but only a near approach to it; or that complete extraction, only approximate, is obtained by percolation. It is thought that in either case the process was carried far enough to show the value of the procedure.

Character of the soils studied

NUMBER	NAME	RESPONSE TO PO_4 FERTILIZER	GENERAL FERTILITY
1C	Yolo silty clay loam	Little	Very good
30	Fresno fine sandy loam	None	Very good
36	Farwell sandy loam	Large	Low
37	Nord sandy loam	Large	Low
38	Vina silty clay loam	Little	Good
40	Altamont-Olympic loam, wash	None	Very high
45	Aledo, Ill., clay loam and rock phosphate	....	Good
46	Aledo, Ill. Same untreated	....	Poor
53	Delhi sand	Some	Fair
59	Aiken clay	Very great	Medium
64	Vina silt loam	Great	Poor
65	Yolo loam	Little	Very high
66	Aiken clay	Great	Medium
68	Tejunga fine sand	Little	Good
69	Sites clay loam	Great	Medium
78	Fine sandy loam	Great	Poor
80	Hanford fine sandy loam	Great	Poor

Equilibrium methods for giving an idea of the available PO_4 in a soil are subject to the general criticism that the effects produced in this way are very unlike those produced by a plant drawing nutrients from the soil in a selective manner. In an equilibrium extraction, some of the products of the action of weak solvents may tend to repress solubility of PO_4, e.g. Ca and Mg brought into solution by weak or dilute acids. This has been pointed out by Teakle (23) and others.

It seems irrational to apply such concentrated acids as have commonly been used, such as strong HCl; 0.2 *N* HNO_3, pH 0.7; or 1 per cent citric, pH 2.1, since plants have no such strong solvent agents at their disposal.

Perhaps the best reason for using equilibrium methods is that they may supply useful indications with the least expense of time and labor. A fair idea of the power of a soil to supply PO_4 may be quickly had in this way, but at the same time the result may give an erroneous notion of the availability to plants of the PO_4 thus extracted.

Equilibrium methods

Ratio of soil to solution 1:5. Usually 40 gm. of soil was placed in a 400-cc. bottle with 200 cc. of solution and agitated in an end over end shaker for three hours or more. The mixture was filtered on Whatman No. 12, 24 cm. folded filters, and after nearly all the liquid had run through, the solution was analysed. PO_4 was determined by the molybdenum blue method about as described by Parker and Fudge (19), pH by color comparison, Ca by turbidity after adding $(NH_4)_2O_x$, Fe by color comparison after adding $K_4Fe(CN)_6$ and HCl.

A single extraction of any soil by any solvent which changes the pH materially gives only a very incomplete picture of the character of the soil in regard to its power to supply phosphate under changing conditions. But by using three or four different concentrations of a dilute acid, much more is learned. In this, it is important to note the pH of the solution removed from the soil. This presumes that only dilute acids are used, so that the pH of the extract never is brought below 2.

In this manner, more than 50 different soils have been examined. A few typical results are presented in table 1, which gives the figures obtained with citric, oxalic, and hydrochloric acids of 0.005, 0.025, 0.050, and 0.100 normalities. This shows the great differences between different soils and also the different results given by the different acids of the same concentration on any one soil. These figures indicate something of the buffer power of the soil, or its power to neutralize acid, how much acid is needed to reduce the pH of the soil to some lower point, and how much PO_4 may be brought into solution at that pH. It is apparent that the amount of PO_4 dissolved is closely related to the pH of the solution when simple acids such as HCl or HNO_3, and probably also CO_2, are used. Citric and oxalic acids form soluble complexes with Fe^{+++}, and other cations, so have greater solvent effect than their concentration of hydrogen ion should give of itself. Oxalic acid is peculiar in that it removes Ca from solution at pH above 3 to 4, thus permitting more PO_4 to remain in solution than would HCl, H_2SO_4, or HNO_3. Also, citric and oxalic acids are not appropriate because they must be removed from the solution before it is tested for PO_4 content by the molybdenum blue method. Carbon dioxide in equilibrium at ordinary atmospheric pressure has too small a concentration of hydrogen ion to be an active solvent. But when used continuously as in percolation with water saturated with CO_2, it has great solvent effect since the products of reaction are continually removed, thus allowing the reaction to proceed to completion in one direction. This largely accounts for the great effects on the soil produced by rain water.

Buffer power of the soil in relation to the solution of soil phosphates by dilute acids. The figures appearing in table 1 show how different is the effect of a dilute acid on different soils. It seems evident that instead of using the same arbitrary concentration of acid on all soils, an amount of acid should be used such that the pH of the extract will be the same for all soils. If this is accomplished the results should be properly comparable. The figures given in table 1 may be plotted so that by interpolation or extrapolation the PO_4 soluble at any definite pH, such as 4, may be inferred. Figure 1 gives such graphs for a few soils, and table 2 gives PO_4 at pH 4 for several soils. These figures seem to give a much better idea of the phosphate-supplying power of the soil than do those found by the use of the same amount of acid for all soils, in which case the pH of the extracts often differs greatly.

There are two objections to this method. Unless two points somewhere near pH 4 happen to be hit in the determinations, the figure inferred for pH 4

may be wide of the truth, and this method requires the preparation and analysis of three or four solutions. To avoid these objections, it was sought to make the extraction by the use of such an amount of acid that the extract would have a pH of approximately 4. This was found difficult to accomplish in a simple practical way because when a soil is mixed with a dilute, highly ionized acid, the pH does not remain at one point for more than a few minutes, and because it is necessary to make some preliminary experiments to indicate about how much acid will be needed to bring the pH of the soil to any definite point.

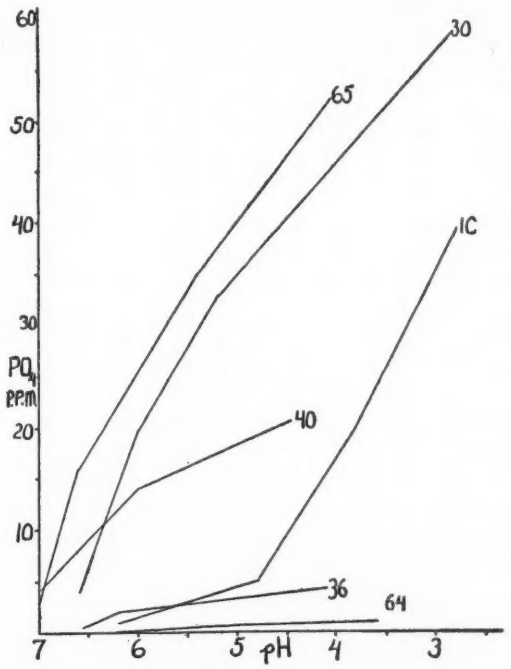


FIG. 1. RELATION OF PO_4 IN DILUTE ACID EXTRACT TO pH OF THE EXTRACT

The figures given in table 3 show how rapidly the solution changes after acid has been added and how greatly soils differ in this respect when the highly ionized, slightly buffered HCl is used. Addition of KCl, suggested by Truog (24), to the acid did not give enough buffer effect to be of any advantage. When citric acid was used, its buffer power made the change in content of PO_4 of the solution much slower, but it is undesirable for reasons stated on page 440. Acetic acid is little ionized, highly buffered, and otherwise an appropriate solvent. Although the PO_4 content of the extract made with this acid is less constant in some cases than when citric acid is used, it seems better adapted

for estimating available PO_4 than any of the other common acids. Oxalic acid, suggested by Vanstone (25), is even less appropriate than citric acid. Some of the results obtained with acetic acid are given in table 4.

TABLE 1

PO_4 and pH in 1:5 equilibrium extracts of soils with citric, oxalic, and hydrochloric acids of four different concentrations

SOIL NUMBER	ACID	0.005 *N* ACID		0.025 *N* ACID		0.05 *N* ACID		0.1 *N* ACID	
		PO_4 p.p.m.	*pH*	*PO_4 p.p.m.*	*pH*	*PO_4 p.p.m.*	*pH*	*PO_4 p.p.m.*	*pH*
1C	Citric	5	5.2	16	4.2	27	3.6	44	3.0
	Oxalic	10	5.2	27	4.4	50	3.3	66	2.4
	HCl	5	4.8	20	3.8	40	2.8	40	1.5
30	Citric	24	4.2	33	3.3	40	2.9	57	2.6
	Oxalic	40	3.9	66	2.4	80	1.8	80	1.4
	HCl	40	4.8	80	2.8	80	1.5	80	1.5
65	Citric	40	5.2	50	4.2	66	3.6	66	3.0
	Oxalic	40	5.3	44	4.0	56	3.0	80	2.0
	HCl	40	5.2	56	3.0	80	2.0	80	1.5
38	Citric	....	...	10.0	4.4	13	3.7	20	3.0
	Oxalic	....	...	8.0	4.8	20	3.6	50	2.4
	HCl	....	...	3.2	4.0	6.6	2.4	10	1.4
64	Citric	....	...	8.8	4.5	13	3.6	22	3.0
	Oxalic	....	...	8.0	5.0	20	3.6	66	2.4
	HCl	....	...	7.2	3.6	10	2.2	13	1.5
35	Citric	....	...	5.6	3.8	9.0	3.2	11.0	2.8
	Oxalic	....	...	2.0	4.4	5.0	3.4	33.0	2.4
	HCl	....	...	0.8	3.2	1.2	2.0	2.4	1.4
59	Citric	0.2	5.2	0.4	3.9	0.3	3.2	0.3	2.5
	Oxalic	0.2	5.0	1.0	4.4	0.4	3.4	1.6	2.5
	HCl	0.1	4.2	0.1	3.0	0.1	2.0	0.1	1.0
37	Citric	1.0	7.5	1.2	7.3	1.6	7.0	10.0	4.4
	Oxalic	1.0	7.5	1.2	7.3	3.2	6.8	11.4	4.5
	HCl	0.6	7.5	1.2	7.0	3.2	5.6	11.4	4.0
36	Citric	....	...	13	4.4	20	3.6	26	3.0
	Oxalic	....	...	16	4.8	50	3.6	80	2.4
	HCl	....	...	8	4.0	20	2.2	40	1.8

Probably a much larger proportion of solvent to soil would make it easier to hold the pH of the extract to some definite point. In table 5 are shown some of the results obtained with 2 gm. of soil to 200 cc. of solution. Although the

concentration of PO_4 in the extract is much higher in the 1:5 extracts, the amount dissolved from the soils is much greater in the 1:100 extracts. The greater proportion of water dissolves much more PO_4 from the soil. In the more dilute extracts the relative supplying power of the different soils is quite different from that found by the 1:5 extraction. But the latter represents much better the actual phosphate-supplying power of the soils as indicated by growth of plants on them.

This brings out the point that in most soils only a small proportion of the phosphate present dissolves in weak solvents at small dilutions. It seems reasonable to think that the nearer the ratio of soil to solution is to the ratio existing in a soil where plants are growing, the nearer will the results for PO_4

TABLE 2

PO_4 in 1:5 equilibrium extract of soils with dilute HCl, at pH 4 by interpolation

FERTILITY OF SOIL	SOIL NUMBER	PO_4 AT pH 4
		p.p.m.
Very fertile	1C	17
	30	44
	40	23
	65	52
Good	36	4.0
	37	11.0
	38	1.5
	68	14.0
Aledo, Ill., and rock phosphate	45	13.0
Aledo, Ill., not fertilized	46	1.4
Very poor	64	1.0
Exceedingly poor	59	0.1
	66	0.1
	69	0.4
	76	0.2

represent the condition with which the plant has to deal. The work of others, as well as some done during this study, shows that the concentration of PO_4 in water extracts of some soils is almost the same regardless of the ratio of soil to solvent until large dilutions are reached. Results obtained in this study are shown in table 6.

The same thing is shown in table 7, giving the results from extracting several soils with dilute acetic acid with four different ratios of soil to solvent. In this experiment, soils 64, 38, 89B, and 91A gave somewhat the same concentration of PO_4 in the solution whether the ratio of soil to solution was 1/5 or 1/40.

Soils 1C, 30, 36, 68, 75, and 80 show increasing amounts of PO_4 extracted from the soil as the ratio of solvent to soil is increased, yet the increase in PO_4

is not equal to the increase in dilution. In table 5 are some figures found by a dilution of 1/100, and the other extreme is shown in table 8, with a ratio of 2/1. Pot cultures show that the PO_4-supplying power of the soil is much better rep-

TABLE 3

Change in pH and PO_4 with change in time after acid has been added

120 gm. soil shaken with 600 cc. of solution

SOIL NUMBER	0.1 *N* HCl ADDED	TIME FOR REACTION	SOLUTION AFTER FILTERING	
			pH	PO_4
	cc.			*p.p.m.*
1C	300	10 minutes	2.05	50
		1 hour	2.21	50
		5 hours	2.62	29
		24 hours	3.13	10
		72 hours	3.38	4
30	120	10 minutes	2.05	40
		1 hour	2.17	66
		5 hours	2.31	100
		24 hours	2.53	111
		72 hours	2.70	117
35	200	10 minutes	2.07	0.88
		1 hour	2.57	0.58
		5 hours	3.19	0.40
		24 hours	3.54	0.28
		72 hours	3.54	0.20
36	300	10 minutes	2.09	25.0
		1 hour	2.39	25.0
		5 hours	2.66	15.0
		24 hours	3.00	5.0
		72 hours	3.21	2.4
38	170	10 minutes	2.79	4.8
		1 hour	3.17	2.8
		5 hours	3.73	1.7
		24 hours	4.09	0.8
		72 hours	4.05	0.7
64	270	10 minutes	2.01	11.4
		1 hour	2.31	8.8
		5 hours	2.55	4.8
		24 hours	2.87	1.6
		72 hours	3.12	1.1

resented by the figures given in table 7. The chief reason for using a 1:5 ratio instead of 2:1 of soil and solvent, is that it is much more convenient, and still the dilution is not so great that the results are not applicable.

TABLE 4

Change in pH and PO_4 with time after acid has been added

80 gm. soil shaken with 400 cc. solution

SOIL NUMBER	TIME FOR REACTION	0.1 *N* CITRIC ACID	pH	PO_4 IN SOLUTION	0.1 *N* ACETIC ACID	pH	PO_4 IN SOLUTION
		cc.		*p.p.m.*	*cc.*		*p.p.m.*
1C	5 minutes	70	4.13	8.0	250	....	.....
	75 minutes		4.29	11.4		4.04	12
	5 hours		4.46	11.4		4.04	10
	16 hours		4.58	11.4		4.09	8
	48 hours		4.90	11.4		....	.....
36	5 minutes	70	4.18	3.4	270	....	.....
	75 minutes		4.32	6.6		4.01	6.4
	5 hours		4.40	6.6		3.99	4.4
	16 hours		4.51	6.6		4.05	2.8
	48 hours		4.70	6.6		....	.....
38	5 minutes	70	4.13	1.4	220	....	.....
	75 minutes		4.32	2.3		4.05	1.44
	5 hours		4.51	2.4		4.09	1.24
	16 hours		4.74	2.4		4.13	1.14
	48 hours		5.17	1.8		....	.....
30	1 hour		....	....	100	3.97	19
	5 hours		....	....		3.97	22
	24 hours		....	....		4.05	25
64	5 minutes		....	....	220	3.96	3.2
	1 hour		....	....		4.05	2.0
	5 hours		....	....		4.03	1.2

TABLE 5

PO_4 extracted from soils by dilute acetic acid at approximately pH 4

2 gm. soil to 200 cc. solution shaken 1 hour

SOIL	0.1 *N* H Ac IN 200 CC.	pH	PO_4 IN SOLUTION
	cc.		*p.p.m.*
1C	10	4.1	4.0
30	5	4.1	2.4
36	10	4.1	2.4
37	20	4.2	2.9
38	10	4.0	1.2
89B	5	4.0	1.2

The important points in the preceding discussion may now be summed up to show what facts and conditions should be considered in devising a method for

TABLE 6

PO_4 in equilibrium extracts of soils with several different proportions of ordinary distilled water

SOIL NUMBER	RATIO OF SOIL TO WATER									
	1/1	1/2	1/4	1/10	1/20	1/50	1/100	1/500	1/1,000	1/2,500
	PO_4 p.p.m. in solution									
1C	0.20	....	0.20	....	0.20	....	0.16	0.20	0.12	0.02
30	4.40	....	3.60	....	2.00	....	0.70	0.16	0.02	0
36	....	0.50	....	0.40	....	0.24	0.20	0.16	0.08	0
37	....	0.50	....	0.60	....	0.28	0.12	0.10	0.04	0
38	0.32	....	0.40	....	0.12	....	0.20	0.12	....	0.06
35	....	....	0.04	....	0.04	....	0.06	0.10	....	....

TABLE 7

PO_4 in acetic acid extracts of soils with various weights of soil to 200 cc. of solvent mixture, shaken one hour before filtering

SOIL NUMBER	SOIL	0.1 *N* H Ac	pH	PO_4 IN SOLUTION	SOIL NUMBER	SOIL	0.1 *N* H Ac	pH	PO_4 IN SOLUTION
	gm.	*cc.*		*p.p.m.*		*gm.*	*cc.*		*p.p.m.*
1C	5	30	3.97	6.8	68	5	25	3.75	3.0
	10	46	3.97	8.8		10	35	3.71	4.4
	20	77	3.95	11.4		20	55	3.67	5.4
	40	140	3.95	13.2		40	95	3.65	7.2
30	5	21	3.85	6.0	75	5	30	3.90	12.0
	10	28	3.83	9.0		10	45	3.96	16.0
	20	40	3.85	14.5		20	75	3.92	27.0
	40	65	3.85	25.0		40	140	3.90	40.0
64	5	29	3.92	3.1	89B	5	20	3.85	1.4
	10	43	3.94	2.7		10	25	3.73	1.8
	20	70	3.92	2.2		20	30	3.97	1.2
	40	125	3.90	2.2		40	40	4.01	1.1
38	5	35	3.94	2.0	91A	5	20	3.99	1.4
	10	50	3.96	2.0		10	27	4.07	1.2
	20	85	3.92	2.0		20	42	4.01	1.0
	40	150	3.92	2.0		40	70	3.97	1.0
36	5	30	3.96	3.6	92A	5	23	4.01	4.4
	10	46	3.96	4.8		10	30	4.05	3.6
	20	80	3.90	6.2		20	45	4.03	2.7
	40	145	3.92	8.0		40	73	4.05	1.5
80	5	30	4.16	6.0		..	..	....	....
	10	45	4.23	9.0		..	..	....	....
	20	75	4.25	14.5		..	..	....	....
	40	140	4.29	20.0		..	..	....	....

determining availability of soil phosphates by equilibrium extracts and to give results numerically properly comparable:

Soils differ in power to neutralize acids, "buffer power." Acids bring into solution cations which tend to remove PO_4 from solution between pH 3 and 8.

Chemical reagents have not the selective power of plants, and plants have no strong solvent powers similar to strong acids.

The best kind and strength of acid for estimating the availability of soil phosphates are not known, but it should not be a strong, highly ionized, slightly buffered acid, since such will not hold the pH or PO_4 constant for more than a few minutes.

A highly buffered acid makes it much easier to hold a constant pH and approximately constant PO_4, though in any case PO_4 in solution changes even if pH is held constant, but citric and oxalic acids are not appropriate because they form soluble complexes with Ca, Mg, Al, and Fe, thus preventing them from having their normal effect on solubility of PO_4 at the corresponding pH.

TABLE 8

Equilibrium extracts

200 gm. soil with 100 cc. dilute acid

SOIL NUMBER	0.1 *N* HCl USED	pH OF EXTRACT	PO_4 IN EXTRACT	TIME ALLOWED FOR REACTION
	cc.		*p.p.m.*	*hours*
1C	60	4.0	1.6	15
30	30	4.0	40.0	4
35	50	3.7	0.2	4
36	100	4.4	1.3	15
37	60*	5.2	2.6	15
38	55	4.8	0.4	15
64	75	4.2	0.3	15
76	30	3.4	0.8	4
79	50	3.8	0.2	4

* *N* HCl.

Acetic acid has not these defects, is well buffered, and is convenient.

To be properly comparable, all extracts should have approximately the same pH, say 4, and all other conditions of making the extracts, such as time, volume of solution, and method of shaking, should be similar.

Time required to reach equilibrium is not known but if 24 hours be taken arbitrarily, it will be sufficient for most soils and the results will be comparable for all.

The amount of acid needed for any particular soil must be found by experiment.

Most previous investigators have not controlled these conditions adequately in order to obtain properly comparable results.

To avoid these difficulties as much as possible, the following described procedure is proposed as being practical, easily executed, not very time-consuming or expensive, and as giving results properly comparable, as well as may be expected of any empirical procedure.

Availability test for soil phosphate. A preliminary test is made to learn ap-

proximately how much acid is needed to bring the soil to pH 4. Place 10 gm. of soil in a 100-cc. bottle with 10 to 20 cc. of water. Close the bottle with a soft rubber stopper and shake vigorously a few seconds. Remove the stopper and press the end against a white porcelain plate, making a mud spot. Place a drop of suitable indicator on the mud spot. This gives a good indication of the pH of the soil. Now add a little 0.1 *N* HAc to the mud in the bottle, shake again, make another mud spot, and determine the pH. In this way, continue until a pH of 4 is obtained. This requires only a few minutes. Next calculate how much acid will be needed to bring 40 gm. of soil to pH 4. To each of three 300-cc. bottles add 40 gm. of soil and 200 cc. of dilute acid. One bottle should have about half as much acid as is calculated to bring the soil to pH 4, one bottle should contain the estimated amount and the other considerably more than that amount of acid, but the total liquid should be the same in all three.

Shake the bottles in an end over end shaking machine for 5 hours, let stand over night, then shake again for 3 to 4 hours. Shaking by hand is much less effective, and unlikely to give comparable results. After the shaking is finished, pour the contents of the bottles upon fluted filters. The filters should be previously moistened with dilute HCl and washed free of acid by water, so that they will not change the pH or PO_4 content of the extract. Some of the first of the filtrate is rejected. After the remainder is collected, the pH is determined and the PO_4 is estimated by the molybdenum blue method. Parker's (19) procedure is followed.

In this way, three values of pH and PO_4 for each soil are found. These figures may be plotted; then from the graph, the PO_4 of the soil at exactly pH 4 may be read off.

This test gives information in regard to the buffer power of the soil, how it will be affected by acid, and how much PO_4 will be dissolved at pH 4 or some other convenient point.

Rate of solubility curve. By using several different ratios of soil to solvent, Vanstone (25) derives from the results a curve indicating the relative availability of soil phosphate. In his examples, the chemical tests seem to agree fairly well with field results. Similar results are given by Simon (22). In applying this method to several of the soils used in this work the results do not show the same availability of soil PO_4 as is shown by pot and plot tests with plants. The laboratory results are set out in table 6. Just as in other equilibrium studies, the figures obtained for most soils show fairly well the relative availability of the soil PO_4. But some marked exceptions with all these methods greatly reduce the value of the results as a means of estimating the fertility of an unknown soil. In this respect, the Vanstone method seems no better than most other equilibrium methods. In all the modifications of this method here tried, the results obtained for soils 38, 64, and 80 do not agree with results of pot cultures. In the latter, soil 38 has generally shown a good availability of PO_4 to tomatoes, alfalfa, and barley, whereas soils 64 and 80 fail to give satisfactory

crops without added PO_4, yet the chemical equilibrium tests indicate that these soils contain more avilable PO_4 than soil 38.

Percolation methods

The percolation method of extracting PO_4 from a soil is more like the action of plants than the equilibrium method, since it removes from the soil the products of the action of the solvent, and thus permits the reaction to go toward completion in one direction. In beginning this study, it was hoped that percolation methods would give some measure of the power of a soil to renew PO_4 in the soil solution after the easily soluble PO_4 had been removed. J. W. Tidmore and L. Meyer, working independently in this laboratory, at about the same time sought to attain the same end by different methods (see p. 461).

The methods, described in the following, have been in use here for three years, have been applied to hundreds of different soils, and have given results in most cases according fairly well with the character of the soil as shown by growth of plants in pots or in the field.

Two concentrations of acid, 0.001 *N* and 0.05 *N*, have been used. The procedure is essentially the same with both, though the apparatus used with the more dilute acid is capable of much more precise control so that the results are more easily reproducible.

The details of procedure are about as follows, so far as the soil is concerned.

Twenty grams of the soil is placed in a filter tube 48 mm. in diameter. The soil rests on a bed of filter paper pulp 5 to 8 mm. thick, supported on a filter plate. If the soil is fine in texture, some acid-washed white sand is mixed with it to aid in percolation. This sand is quite fine, nearly pure quartz. It has a slight fixing power so that a small amount of PO_4 is retained by the sand when a dilute solution is passed through it. However, it was found that after 1 liter of 0.001 *N* HCl had been passed through it, practically the whole 0.2 mgm. of PO_4 added to the sand was recovered. So there is no fear that the sand will retain any of the PO_4 extracted from the soil.

When the filter tube with the soil and with added sand, if necessary, is set up it is connected with an elevated reservoir of the dilute acid by a pressure tube about 1.6 m. long, and the acid is allowed to percolate through the soil at the rate of about 1/3 liter an hour continuously for about 20 hours until very little PO_4 is found in the percolate or until a definite volume of percolate has been collected. Originally the percolation was continued until nearly complete extraction of the PO_4 soluble in that reagent was obtained. Lately the procedure has been standardized so that 7 liters of percolate are taken for each soil.

Percolation with 0.001 N *HCl.* With this procedure, the percolate is collected in a train of liter bottles in such manner that the contents of the seven bottles represent successive stages in the extraction. The percolates are analyzed separately so that the rate of extraction of PO_4, and the Ca and the pH of each may be determined. When the apparatus is set up and percolation started, it proceeds automatically without attention except to see that the supply reser-

TABLE 9

PO_4 extracted from soils by percolation with 0.001 N and 0.05 N HCl

SOIL NUMBER	ACID NORMALITY	PO_4 IN SUCCESSIVE 1-LITER PORTIONS OF PERCOLATE							TOTAL EXTRACTED	TOTAL IN SOIL	AVAILABLE
		1	2	3	4	5	6	7			
		p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*mgm.*	*p.p.m.*	*per cent*
1C	0.001	1.50	2.65	2.60	2.65	2.50	2.00	1.65	15.75	787	82
	0.05	17.00	1.10	0.5	0.30	0.30	0.20	0.10	19.30	965	
75	0.001	3.60	4.40	4.40	3.20	1.60	0.80	0.52	18.92	946	78
	0.05	18.00	2.70	1.00	0.54	0.54	0.54	0.40	23.76	1,188	
30	0.001	5.00	4.40	2.70	2.00	1.10	1.00	0.90	17.10	855	76
	0.05	20.00	1.00	0.50	0.30	0.30	0.10	0.10	22.30	1,115	
53	0.001	2.10	1.80	1.50	1.20	0.80	0.60	0.5	8.35	417	91
	0.05	6.40	1.60	0.50	0.22	0.20	0.14	0.10	9.16	458	
68	0.001	5.00	6.20	4.40	2.80	2.00	1.40	1.0	22.80	1,140	92
	0.05	22.00	2.00	0.40	0.20	0.10	0.10	0.0	24.80	1,240	
78	0.001	0.14	0.16	0.12	0.08	0.06	0.04	0.04	0.64	32	71
	0.05	0.40	0.16	0.10	0.08	0.07	0.06	0.04	0.91	45	
36	0.001	0.75	1.65	2.00	1.65	1.65	1.40	1.25	10.35	517	77
	0.05	11.00	0.88	0.44	0.34	0.29	0.25	0.20	13.40	670	
37	0.001	1.10	1.15	1.10	1.10	1.10	1.10	1.10	7.75	387	59
	0.05	10.80	1.60	0.31	0.20	0.16	0.12	0.08	13.30	663	
38	0.001	0.40	0.80	1.24	1.44	1.16	0.50	0.40	5.94	297	87
	0.05	4.00	1.00	0.48	0.31	0.25	0.20	0.16	6.40	320	
64	0.001	0.68	1.60	1.60	1.44	0.88	0.88	0.88	7.96	398	56
	0.05	8.00	3.20	0.80	0.70	0.60	0.40	0.40	14.10	705	
80	0.001	0.88	1.76	2.00	2.00	1.60	1.10	1.00	11.00	550	60
	0.05	16.00	2.90	0.20	0.10	0.10	0.06	0.04	19.40	970	
35	0.001	0.02	0.04	0.04	0.04	0.04	0.06	0.07	0.31	15	13
	0.05	0.66	0.44	0.29	0.25	0.25	0.22	0.20	2.31	115	
59	0.001	0	0	0	0	0	0	0	0	0	0
	0.05	0.10	0.04	0.01	0.01	0.01	0	0	0.17	8	
89B	0.001	1.16	2.00	1.36	0.80	0.60	0.54	0.40	7.06	353	44
	0.05	7.20	2.20	1.40	1.30	1.30	2.00	0.90	16.20	810	

voir of dilute acid is kept filled. When one soil is sufficiently extracted, it may be quickly replaced by another, a new set of collecting bottles is set in position and the process continues without further attention.

It is obvious that in order to have truly comparable results with different soils, all variables except the soil, should be kept out of the procedure. This is fairly well done by the apparatus used. It has been more fully described in another paper (13). The rate of flow of the dilute acid through the soil varies somewhat from moment to moment, but averages very nearly 1 liter every

TABLE 10

Analyses of soil percolates made with 0.001 N HCl

PERCOLATE NUMBER	pH	Ca	PO_4	pH	Ca	PO_4	pH	Ca	PO_4	pH	Ca	PO_4
		p.p.m.	*p.p.m.*		*p.p.m.*	*p.p.m.*		*p.p.m.*	*p.p.m.*		*p.p.m.*	*p.p.m.*
	Soil 38			*Soil 64*			*Soil 35*			*Soil 59*		
1	4.0	14	0.16	4.0	14	0.08	3.6	12	0	4.0	20	0
2	3.8	14	1.08	4.0	14	1.32	3.4	16	0	3.6	6	0
3	3.6	22	1.44	4.2	14	2.00	3.3	10	0	3.2	3	0
4	3.4	18	1.44	3.8	14	1.60	3.2	6	0	3.2	0	0
5	3.4	10	1.08	3.4	10	1.32	3.2	2	0.04	3.0	0	0
6	3.2	6	0.56	3.2	6	1.00	3.0	1	0.07	3.0	0	0
7	3.2	6	0.48	3.0	2	0.80	3.0	0	0.07	3.0	0	0
	Soil 1C			*Soil 30*			*Soil 37*			*Soil 80*		
1	6.2	4	1.50	4.6	12	5.00	6.8	5	1.10	5.2	6	0.88
2	5.6	5	2.65	3.3	1	4.40	6.2	7	1.15	5.2	6	1.76
3	4.4	7	2.80	3.2	0	2.70	5.4	12	1.10	4.2	14	2.00
4	4.2	7	2.65	3.2	0	2.00	5.4	15	1.10	3.8	10	2.00
5	4.0	7	2.50	3.0	0	1.10	5.4	12	1.10	3.4	6	1.60
6	3.7	4	2.00	3.0	0	0.95	5.4	10	1.10	3.0	3	1.10
7	3.4	3	1.65	3.0	0	0.90	5.2	8	1.10	3.0	tr.	1.00
	114 mgm. $CaHPO_4$, $2H_2O$			*66 mgm. $Ca_3(PO_4)_2$*			*0.2 gm. white rock phosphate*			*0.2 gm. black rock phosphate*		
1	3.6	..	66.00	3.4	..	40.00	3	6	15.6	3.4	15	25.0
2	3.0	..	6.20	3.0	..	0.36	3	4	10.8	3.0	12	21.0
3	3.0	..	0.96	3.0	..	0.30	3	3	7.3	3.0	8	15.4
4	3.0	..	0.34	3.0	..	0.24	3	..	6.6	3.0	..	13.5
5	3.0	..	0.26	3.0	..	0.20	3	..	6.3	3.0	..	7.3
6	3.0	..	0.24	3.0	..	0.18	3	..	5.6	3.0	..	5.2
7	3.0	..	0.22	3.0	..	0.20	3	..	5.3	3.0	..	3.1

three hours. Starting with 20 gm. of soil, nearly all the PO_4 soluble in 0.001 *N* acid is extracted from good soils by 7 liters of percolate, but not all is removed from some of the soils having the PO_4 in less available condition. The rate of flow being nearly constant, and the aliquots of percolate being of the same volume, the results for different soils are thought to be properly comparable. The figures obtained for a number of soils are set out in table 9, which also

gives the figures found when 0.05 *N* acid was used. The figures reveal the great difference between soils as to solubility of PO_4. Some, such as 1C, 36, 38, 65, have considerable buffer power so that much of the free hydrogen ion of the first liter of acid passing through the soil is neutralized with the result that there is little change in pH of the soil and consequently little PO_4 dissolved. As the buffer effect of the soil is overcome, pH is lowered and PO_4 in the percolate increases to a maximum, which depends on the rate of flow and the

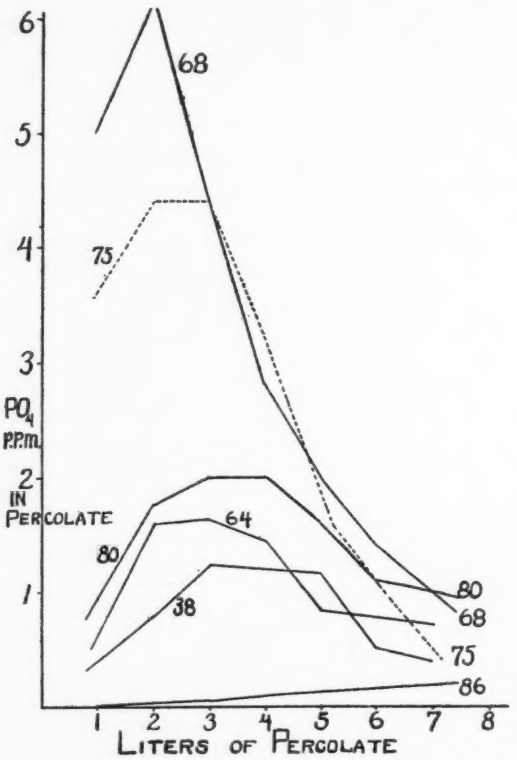


FIG. 2. PO_4 IN EXTRACTS MADE BY CONTINUOUS PERCOLATION WITH 0.001 *N* HCl

character of the soil. Other soils, such as 30, 53, 68, have little buffer power and this is soon overcome by the dilute acid so that the highest concentration of PO_4 is found in the first liter of percolate, and rapidly decreases thereafter. At first, it was thought that this indicated how the soils would respond in supplying PO_4 to a growing crop. Experience has not yet shown whether or not this is true.

In the use of this method, it is a very simple matter to determine Ca by tur-

bidity and pH by color comparison in the separate bottles of percolate. From 1 to 2 hours' time is enough to make all the tests for two soils, in the 14 bottles. This information often helps much to understand the nature of the soil. Table 10 presents some of the figures thus found. Most of the easily soluble or replaceable Ca, presumably Mg also, is soon removed along with the easily soluble PO_4. When the soil contains much $CaCO_3$, this neutralizes the acid and prevents lowering of pH, so PO_4 is not so rapidly extracted. This is shown by soil 37 which contains 1 per cent $CaCO_3$. Some soils such as 35 and 59 contain a fair amount of PO_4, but it is practically insoluble in 0.001 *N* acid. In such soils, usually the amount found in the percolate increases slowly for some time as the volume of percolate increases. In these, it seems probable that the PO_4 is combined with Fe or Al in the soil in such manner that it is not soluble in 0.001 *N* HCl. When the PO_4 is combined with Ca, it is easily dissolved by this acid (table 10, in which the action on $CaHPO_4$ and $Ca_3(PO_4)_2$ and on two rock phosphates is shown). In this work, HCl is the acid used because of its convenience and the easy solubility of its reaction products. HNO_3 works in the same way and is more to be expected in the soil solution, but it is likely to interfere in the colorimetric estimate of PO_4. HCl of 0.001 *N* strength has a pH of about 3, somewhat similar to that of water saturated with CO_2 and perhaps not greatly different from the pH of the sap of some plants. It has very little action on soil silicates or zeolites except to replace imperfectly Ca, Mg, Na and K.

Percolation with 0.05 N *HCl.* This concentration of acid was selected because it seems strong enough to remove from the soil all the PO_4 that plants are likely to be able to extract within many years. It almost completely replaces bases, Ca, Mg, Na, and K. It completely extracts PO_4 from $Ca_3(PO_4)_2$ and from ordinary rock phosphates. It dissolves some iron and silica, usually very little from ordinary soils. In order to carry the extraction of PO_4 to completion with 0.05 *N* acid, the dissolved substances must be removed so that the reaction can go to completion in one direction. This is accomplished by continuous percolation.

The concentration of hydrogen ion in this acid, about pH 1.35, is sufficient to overcome quickly the buffer power of 20 gm. of ordinary soil so that the larger portion of the available PO_4 is removed by the first liter of percolate. Succeeding liters of percolate contain less and less PO_4, as shown in table 9. On account of the rapid removal of the PO_4 by this acid, little useful information is obtained by testing each liter of percolate separately, so the whole is collected together. Some relatively infertile soils still give up appreciable amounts of PO_4 to 0.05 *N* HCl after 7 liters have percolated through 20 gm. of soil at the rate of 200 to 300 cc. an hour. This is true of soils 35 and 64, and of 59 to which considerable amounts of superphosphates have been added. Very little PO_4 is extracted from untreated soil 59. In many cases the amount of PO_4 extracted by percolation with 0.05 *N* HCl fairly well represents the capacity of the soil to supply PO_4 to crops, but perhaps not as well as the 0.001 *N* percolate.

Since carbonic acid is perhaps the most important in its effects of any free acid usually found in the soil, it would seem reasonable to use this agent for extracting PO_4 from the soil. For this purpose, a modification of the apparatus used for percolating with 0.05 *N* HCl was made in order to use water saturated with CO_2 under a head of about 1.5 m. of water. The gas was caused to bubble into the lower end of the column of water which was flowing to the percolator. From the top of this column, the CO_2 passed into the reservoir which supplied the water so that the water was kept saturated with the gas at all times, at that temperature and pressure. The pH of this solution as it passed to the soil in the closed percolator was about 3, like that of 0.001 *N* HCl, but the total acidity, found by titration, was about 0.05 *N*, like that of the HCl used in the same way. In other words, little of the CO_2 was ionized, the solution was highly buffered, and its solvent power approached that of 0.05 *N* HCl. In table 11, column 5, are given a few figures showing the results obtained by the use of this acid. Since it is very inconvenient to use, and the results it gives are no more significant than those obtained with HCl, its use was not long continued. Although the water solution of CO_2 entering the percolator had a pH of about 3, the solutions coming from the percolator, when the pressure no longer confined the gas, had a pH near 5.

TABLE 11

PO_4 extracted from soils by various solvents, and by different procedures

SOIL NUMBER	TOTAL BY FUSION	PO_4 IN SOIL				EQUILIBRIUM WITH WATER, 1:1	PO_4 IN SOLUTION AT 1:5 EQUILIBRIUM WITH ACIDS						
		By hot HCl, 10 per cent	By percolation with				Normality of HCl				Normality of citric acid		
			0.05 *N* HCl	0.05 *N* CO_2	Water, pH 5		0.01	0.02	0.20	1.0	0.025	0.05	0.20
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1C	2,000	1,160	680	660	307	0.18	4	10	50	200	11.4	27	66
30	1,600	1,370	1,197	702	290	8.00	40	80	166	310	35	40	88
35	2,400	1,120	140	0	0	0.12	0.16	0.24	10	44	5.6	8.8	11
36	2,500	1,020	418	420	...	0.30	2.3	9.4	36	160	13	20	36
37	2,400	.....	494	829	...	0.47	0	0.2	25	160	5	....	44
38	2,500	990	320	210	40	0.22	0.8	1.2	13	57	10	13	24
40	3,300	2,720	1,430	1,100	...	1.40	13	20	166	360	33	....	160
45	3,800	.....	1,850	.....	...	0.40	5	13	.....	...	13	....	.....
46	1,600	.....	80	.....	...	0	1.2	2.2	.....	...	5.6	....	.....
59A	2,000	100	tr.	.....	...	0	0	0	0.3	1	0.6	0.7	2
64	1,700	1,180	650	360	63	0.16	0.4	2	50	100	10	13	27
65	2,800	.....	1,170	1,170	...	3.4	35	60	200	280	80	....	182
69A	1,600	1,210	12	0	...	0.14	0.3	0.4	1.4	100	2.3	....	3.2
78A	450	340	50	13	...	0.20	1.4	1.8	8	22	....	....	6.6
80	1,150	950	795	738	128	0.30	2.3	27	118	200	....	....	....

More dilute solutions of CO_2 in water were tried but their solvent power was so little that they seemed impractical. Water containing CO_2 at pH 5, which

is about that of ordinary distilled water, must be percolated through a mass of 20 gm. of good soil for many days in order to extract as much PO_4 as will be removed by 7 liters of 0.001 *N* HCl in 15 hours (table 12). For the practical purpose of estimating the easily available PO_4 in a soil, water containing none or only small amounts of CO_2 is very ineffective. A greater concentration of hydrogen ion than can be had in this way is necessary to produce much solvent effect.

In table 11 are presented the results of analyses of several different soils by a number of different procedures with various solvents of different strengths. There are three subdivisions of the table; first, the total PO_4 found by fusion, and by hot 10 per cent HCl; second, PO_4 found by percolation; and third, the PO_4 found in equilibrium extracts. The figures are thus assembled to facilitate comparisons of the different methods. In most cases, the total PO_4 found by fusion and that extracted by strong hot acids, has little relation to the value of the soil as shown by plants, so that such determinations are generally useless

TABLE 12

*PO_4 extracted by percolating with ordinary distilled water**

SOIL NUMBER	PO_4 IN SOIL
	p.p.m.
1C	307
30	290
35	0
38	40
64	63
80	128

* The same apparatus and procedure were used as with 0.05 *N* HCl.

Volume of percolate, 6–7 liters. In all except 35, there was still much PO_4 in the last percolate, showing that the soil was not nearly exhausted of water-soluble PO_4 by this method.

for indicating the fertility of the soil. Equilibrium extracts with dilute weak acids supply much more useful figures. The best indication is the result found by percolation with very dilute acids. This will be considered in more detail later.

Relative solubilities with different solvents. The amount of PO_4 extracted from soil by any of the aforementioned methods, either by equilibrium or by percolation, does not always indicate whether or not the PO_4 thus obtained will be supplied to plants by the soil in such manner or rate that it will support good growth of crops. Other students of this subject have reached a similar conclusion. To provide a more reliable or adequate notion of availability, the factor "relative solubility" has been introduced. One of its most prominent advocates is Lemmermann (14), who has contributed numerous papers on this subject. He extracts soil with hot 10 per cent HCl and with 1 per cent citric acid. When the PO_4 extracted by the latter is less than 25 per cent of that dis-

solved by the HCl he considers that the soil is likely to respond to phosphate fertilizers. In this laboratory, a number of soils treated by this method gave results not in accord with their behavior in pot cultures. It may be that the amount and concentration of the acids used by Lemmermann are not well adapted to our soils. The principle seemed worthy of further study. It was applied to a number of combinations of different solvents without giving results of much value, except in one case. The results are given in table 13.

The Lemmermann numbers shown in this table in the column headed 100 C/B show some of the soils in their proper relations, but others are far from correct; e.g. 59, 64, 78, the poor soils, are made to appear better than they really

TABLE 13

Relative solubilities of soil phosphate

SOIL NUMBER	RELATIVE SOLUBILITY		
	$\frac{100\ C}{B^*}$	$\frac{100\ D}{A}$	$\frac{100\ E}{D}$
1C	5.7	48.0	82
30	6.4	70.0	76
35	1—	6.0	7
36	3.5	27.0	77
38	2.4	13.0	87
40	5.8	43.0	60
53	5.6	57.0	91
59	2.0	0.0	0
64	2.3	39.0	56
69	0.2	0.7	0
78	2.0	10.0	71
80	...	84.0	60

* 100 *C/B* is Lemmermann's factor of availability.

A = p.p.m. PO_4 in soils found by fusion (see table 11).

B = p.p.m. PO_4 in soils found by equilibrium hot 10 per cent HCl (see table 11).

C = p.p.m. PO_4 in soils found by equilibrium 0.2 *N* citric acid (see table 11).

D = p.p.m. PO_4 in soils found by percolation with 0.05 *N* HCl (see table 9).

E = p.p.m. PO_4 in soils found by percolation with 0.001 *N* HCl (see table 9).

are. In the column headed 100 D/A the valuations are more nearly right, although in this, soils 38 and 64 are not in proper relation to each other. In the column headed 100 E/D, 38 and 64, as well as all the others, receive correct values.

Relative solubility of soil PO_4 in 0.001 N *and in 0.05* N *HCl, by percolation.* In all cases so far observed, it is found that if the PO_4 extracted by percolation with 0.001 *N* HCl is less than half as much as is found by similar treatment with 0.05 *N* HCl, the soil is likely to be deficient in power to supply phosphate to plants. On the other hand, good soils give up nearly as much PO_4 to the weaker as to the stronger acid. The results for a number of soils are given in table 9,

in the last column of which is shown the percentage of PO_4 by percolation with 0.001 *N* HCl of the amount found by 0.05 *N* HCl. This gives soils 64 and 80 a low ratio of availability of PO_4, although the amounts extracted are higher than for soil 38, which gives good results in pot cultures without added PO_4, whereas 64 and 80 require phosphate in order to produce good crops. When the absolute amount of PO_4 extracted by either of these acids is very low, as in soil 78A, crops respond to added phosphate even though the relative solubility of that originally present is high.

TABLE 14

Phosphate-supplying power of soils

As related to particle size—per cent clay × p.p.m. PO_4 extracted with 0.05 *N* HCl by percolation

SOIL NUMBER	CLAY	PO_4	CLAY × PO_4
	per cent	*p.p.m.*	
1C	42	680	28,560
21	5	525	2,625
30	7	1,197	8,400
35	29	140	3,060
36	30	418	12,540
37	39	494	20,000
38	52	320	16,640
40	31	1,430	44,330
44A	40	100	4,000
53A	4	500	2,000
54A	42	175	7,350
55A	37	860	31,820
56A	40	490	19,600
59A	48	tr.	48
64	10	350	3,500
65	32	1,170	37,440
66A	42	6	288
68A	12	1,100	13,200
69A	50	12	600

Amount of phosphate in various sized particles

An attempt to explain the relative fertility of soils 38 and 64 on the basis of the amount of PO_4 in large and small sized particles gave no useful information. The soils were separated into sand, silt, and clay fractions by sedimentation in water. The PO_4 in the various fractions was determined but the figures obtained were so similar for the two soils that the differences seemed inadequate to explain the great difference between the two soils respecting available phosphate as indicated by the growth of plants.

It is evident that the physical texture of a soil may greatly affect the availability of the soil phosphate. A fine textured soil has vastly more points of contact for plant roots than a coarse soil, so that a much lower concentration of

PO_4 in the fine soil may furnish a more adequate supply to plants than would a coarse soil having a much higher content of PO_4 in its larger particles.

Failyer, Smith and Wade (10) indicate that in most of the soils examined, the concentration of PO_4 in various sized particles is greater as the size of the particles is smaller.

An attempt was made to correlate the availability of soil phosphate with the proportion of fine material in the soil. The percentage of clay in the soil was multiplied by the number of parts per million of PO_4 found by percolation with 0.05 *N* HCl. In general, the higher the figure thus obtained, the greater is the amount of avilable PO_4 in the soil. But the availability of PO_4 in some sandy soils such as 30 and 68, is much underestimated by this method, whereas soils 38 and 64 receive a relatively proper value. The figures obtained by this calculation are shown in table 14.

TABLE 15

Comparison of phosphate extracted by equilibrium and by percolation

SOIL NUMBER	PO_4 IN SOIL					
	Equilibrium extracts, 1:5 with			1:10 with 0.2 *N* HNO_3, Fraps method	Percolation extracts, with HCl	
	0.02 *N* HCl	0.20 *N* citric	1.0 *N* HCl		0.001 *N*	0.05 *N*
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1C	50	66	200	400	787	965
30	166	88	310	1,120	855	1,115
35	10	11	44	80	15	115
36	36	36	160	220	517	670
37	25	44	160	250	387	663
53	100	44	160	500	417	458
59	0.3	2	1	2	0	8
38	13	24	57	80	297	320
64	50	27	100	270	398	705

Relative amounts of phosphate extracted from soils in equilibrium extracts compared with amounts found by percolation with different acids

The data shown in tables 11 and 12 permit a comparison better shown by recombination of the figures in table 15.

It is apparent that the amount of PO_4 extracted increases as the strength of the acid is increased and that very much more PO_4 is obtained by percolation with the dilute acids than in equilibrium extracts made with much more concentrated acids. Exceptions are soils 35 and 59A which have relatively very little available phosphate. Such soils would show no available PO_4 to the dilute acid used in percolation if it were not for the large volume of acid used in percolation.

It appears to be a general law with respect to solubility of soil phosphate that PO_4 dissolved increases as concentration of hydrogen ion increases, and also as the volume of solvent is increased.

From table 11, it may be seen that there is no relation between the total PO_4 in a soil and the available PO_4 extracted by dilute acids.

Effect of several salts on solubility of soil phosphates

To 100 cc. of water were added 50 gm. of soil and 1 gm. of the salt. After being shaken one hour, the mixture was filtered and the filtrate tested for PO_4. Soils 1C, 36, 37, 38 were used in the experiments. When $FeSO_4$, $CuSO_4$, and $CuCl_2$ were used, no PO_4 was found in the filtrates.

With NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, $CaCl_2$, $CaSO_4$, $BaCl_2$, NaCl, Na_2SO_4, KCl, and K_2SO_4 there was about as much PO_4 in the extracts as with distilled water alone. Ammonium oxalate and ammonium citrate gave extracts containing about 10 times as much PO_4 as did distilled water.

There seemed to be no useful information obtained in this way, so the study was not long continued.

METHODS PROPOSED BY OTHERS

In the course of this study, several methods proposed by others have been studied briefly. The work of von Wrangell and collaborators (27, 28, 29, 30, 31) is most instructive. Time and suitable equipment have not been available to the writer to repeat or verify the very interesting, painstaking, and fundamental work of these investigators in respect to soil phosphates and their availability to plants.

Von Wrangell's work

Shortly after the main group of papers from these workers were published, there appeared in *Chemical Abstracts* brief mention of them, but these abstracts did not make evident the importance of the work done. Indeed, it seems probable that few except German workers in this field have yet heard of, or become impressed by, this work. The writer did not know of it until after the work here reported was done. The conclusions of von Wrangell seem to be supported by such work done in our laboratories as has any bearing on the subject.

The chief factors to be considered in evaluating the ability of a soil to supply PO_4 to growing plants have been very well ennumerated by von Wrangell (27, p. 637): (*a*) The kind of plant, (*b*) presence of lime salts, (*c*) effects of electrolytes and organic substances in the soil, (*d*) the reaction and absorbtive power of the medium in which the plant grows, (*e*) action of microflora. Also it is important to know the time rate at which a soil will regain its original concentration of PO_4, after it has been depleted by extraction with water or by growing plants.

In executing the von Wrangell method, 1 gm. of soil is shaken five hours with 100 cc. of water. The solution is clarified by centrifuging, the clear fluid is siphoned off, and the soil is again shaken with 100 cc. of water as at first, and thus a second extract is obtained. Sometimes further extractions are made in the same manner.

The PO_4 found in the two extracts is designated a and b, then by the formula $a^2/a\text{-}b = x$, is found the total available PO_4 in the soil. If the necessary machines are available the method is short, simple, and convenient. Prof. von Wrangell states that the results obtained are in good accord with the results of pot cultures and field tests.

The writer attempted to obtain similar results by separating the soil extract by filtering, as a suitable centrifuge was not available. This makes the method tedious and less exact than that proposed by von Wrangell, but the results seemed to agree, for most of the soils tried, with the known character of the soils in respect to capacity of the soils to supply phosphate to plants. If this method is found by general experience to prove as reliable as its author predicts, it will, perhaps, replace most other methods now in use.

For estimating the availability of phosphate in calcareous soils, Das (6) has suggested the use of potassium carbonate. Such a reagent may hydrolyze iron and aluminum phosphates, making PO_4 soluble, also replacing Ca in $CaHPO_4$, thus bringing PO_4 into solution. Such an alkaline reagent also dissolves much organic matter, including some organic phosphorous. It is difficult to separate organic from inorganic phosphorous, also the solution is troublesome to prepare for analysis by the molybdenum blue method. Some trials of the method in this laboratory indicated that the results obtained by it have little relation to availability of the phosphate in nearly neutral soils.

The Neubauer (15) method for determining the availability of soil phosphate has not been investigated during this study. It is a plant culture, not a chemcal method. A good comparison of the Neubauer and Lemmermann methods is given by Engels (9) and by Blanck (3). In this country, Neubauer's method for potassium has been studied by Ames and Gerdel (1), and by Haley and Holben (12). As applied to phosphate, there seems to be no published report of work with the method in this country.

Arrhenius (2) proposes to extract the soil with a 1 per cent solution of NaCl containing enough H_2SO_4 to make the solution about 0.002 N in hydrogen ion. As might be expected, the writer found that the PO_4 thus extracted is about the same as if the dilute acid alone were used. This method does not give proper relative values to the power of the soils examined to supply plants with available PO_4.

Dirks and Scheffer (7) add to 100 gm. of soil, 1 gm. $CaCO_3$ and 250 cc. water, then pass CO_2 through the mixture. After some hours, PO_4 is determined in the filtrate. The results obtained in this laboratory by this method were not in agreement with the results shown by plants on the same soils.

Christensen (5) has proposed the use of Azotobacter as an indicator for availability of soil phosphate. His method has been modified and used by Niklas and others (16, 17, 18). A trial of it in this laboratory failed to give useful results. Yet Winogradsky (26) says it gives reliable results in 85 per cent of the tests.

Dyer (8), in 1894, proposed 1 per cent citric acid as an agent for determining available soil PO_4. Much useful information has been obtained in this way, yet the results are not always satisfactory.

Many investigators [notable among them is Fraps (11)] have used 0.2 *N* HNO_3 for determining the availability of soil phosphate. Some have used much stronger acids, e.g. Lemmermann who used hot 10 per cent HCl compared with 1 per cent citric acid to give his factor for "relative solubility" as already explained (p. 455). To the writer, it seems that the use of so drastic a reagent as hot 10 per cent HCl to extract available PO_4 from soil is unlikely to indicate the behavior of the soil with growing plants.

The opposite extreme is found with those who use water only to determine PO_4 is soil. Various ratios of soil to water have been tried, all the way from the displaced soil solution as obtained by Burd and Martin (4), to the 1 to 100 ratio used by von Wrangell. Undoubtedly the soil solution indicates what the plant has to deal with at the time the extract is made, but since the soil solution may change from day to day, it does not show what the plant can obtain from the soil over a considerable period of time. This might be expected, since only a small amount of soil phosphate which is available to plants from soils having a good supply of available phosphate, is dissolved in the soil solution at any one time. The same is probably true in regard to soil extracts made with larger ratios of water to soil, unless it be that when the ratio is wide, as in the method of von Wrangell (1 soil to 100 water), all the easily available PO_4 is brought into solution.

Meyer, a collaborator with von Wrangell (31), obtained somewhat useful results in this laboratory in 1927 by making repeated extractions of the same small portions of soil with 100 times as much water, a variation of the von Wrangell method. The plotted results gave a curve indicating fairly well the availability of the soil phosphate.

At about the same time, J. W. Tidmore in this laboratory made successive diffusions of a small amount of soil in collodion bags suspended in water, by the method of Pierre and Parker (20). The amount of PO_4 found in the successive diffusates was plotted to produce a curve which indicated fairly well the ability of the soil to supply phosphate to plants. The process was prolonged and tedious, though not requiring a great deal of time or attention from the operator. Much time was required because a considerable fraction of the PO_4 dissolved by the water remained in the colloidon sack with the soil each time when the diffusate was removed from the outside container. Although the figures obtained by Meyer and by Tidmore in most cases gave a useful indication of the power of the soil to supply phosphate to plants, the results were not always in accord with the growth of plants in those soils as related to available phosphate.

Apparently no one of the published methods has been found always reliable, so the search still continues.

CONCLUSIONS

In the opinion of the writer, a satisfactory estimation of the availability of soil phosphate by extraction with any one solvent of whatever strength will not, in some cases, be possible. Relative solubility and the total PO_4 dissolved in two solvents of quite different strength, but neither of them strong enough to cause much decomposition of the soil, provide figures much better indicating the capacity of the soil to supply plants with phosphate.

A fairly reliable estimate of the phosphate-supplying power of an unknown soil may be most easily and quickly obtained by analysis of the extract made by the aid of a dilute acid which has been added in such amount that the extract will have approximately pH 4. When there is some uncertainty in regard to the availability of the phosphate thus found, the more certain, as well as more laborious, method of "relative solubility" should be applied.

The equilibrium test will at once indicate the very poor and the very good soils, with the least time and expense. The percolation tests will give more reliable information in uncertain cases.

The only certain means of determining the response of a soil to fertilizers lies in the actual trial with plants in greenhouse or field.

SUMMARY

Some reasons why a satisfactory estimation of the availability of soil phosphates by chemical methods is difficult are:

Phosphate found in soils is mostly present in relatively slightly soluble combinations, so that the concentration in the soil solution is never high.

Plants have selective action in absorption of nutrients, and also it seems probable that plants are able to take up ions such as PO_4, K, perhaps others from films of solution not represented by solutions prepared in the laboratory.

No chemical agent can imitate these effects of plants on soils.

Many soils have such high fixing power that an easily soluble phosphate added to them is quickly fixed, thus becoming more or less unavailable to plants.

Deficiency of other necessary plant nutrients in the presence of sufficient phosphate, or presence of excessive amounts of soluble salts or toxic substances in the soil, may cause the failure of plants.

Test of a soil some time after phosphate has been added and after plants have grown on it subsequent to addition of the phosphate cannot show the condition of the soil with which the plant had to deal at the start.

Equilibrium, 1:5 extracts of soils with dilute acids provide the simplest and quickest means of obtaining some idea of the available phosphate, although such extracts do not always give a correct idea of the relative power of different soils to supply phosphate to plants. Extracts made with three or more different concentrations of an acid give a much better picture of the available PO_4 than is obtained by any single extract. Extracts thus made show only the PO_4 available at the time of extraction, not the relative supplying power of the soil for any great length of time.

Citric and oxalic acids, because they form soluble complexes with Fe, Al, Ca, and Mg (the cations which tend to repress solubility of PO_4), are not appropriate for determining the availability of soil phosphates.

A solution of CO_2 in water would be very appropriate for the purpose if it were easily possible to duplicate conditions at will, but its application is too difficult.

Dilute K_2CO_3 hydrolyzes some phosphates and thus brings PO_4 into solution, but the results do not seem to have much bearing on availability.

If results of tests of different soils are to be compared, the buffer power of the soil must be reckoned with. The amount of acid used in making an extract should be varied according to the buffer power of the soil so that the extracts of all soils will have the same pH, e.g. 4. This means that some soils will need two or three times as much acid as others to have an extract with pH 4.

Since it is difficult to prepare a soil extract of exactly pH 4, or other definite figure, the PO_4 dissolved at any such definite point may be found exactly, by making three extracts with three different concentrations of acid, plotting the results and from the graph finding the PO_4 at the desired pH. For this purpose, a highly buffered acid is desirable. Acetic is very appropriate, much better than HCl.

The amount of PO_4 dissolved increases as the volume of solvent is increased, up to a large dilution. Water extracts of some soils have almost the same concentrations of PO_4 regardless of the volume of water used, up to a dilution of 100 or more water to 1 soil.

The results of such equilibrium extractions seem to be more in accord with plants' response the nearer the proportion of water to soil is to that in the actual soil. But since such extracts are difficult to prepare, a ratio of 1 soil to 5 water serves very well and is more convenient.

Vanstone's "rate of solubility curve" does not in all cases express the plant availability of soil phosphate. It seems to offer little advantage over other equilibrium methods.

Percolation methods of making soil extracts resemble the action of a plant more than equilibrium methods, yet do not show the power of the oil to continue supplying PO_4 so well as was expected and hoped. In these methods the soil is percolated slowly with very dilute acid till most of its soluble PO_4 is removed. An automatic apparatus for percolation has given very good results. Curves formed by plotting the results from percolation extracts are characteristic of the soil's individual power to supply phosphate.

Percolation with 0.05 *N* HCl is supposed to dissolve from a soil all the PO_4 that may be expected to be avilable to plants for many years.

Carbonic acid, 0.05 *N*, has much the same solvent power as HCl, but is very inconvenient.

Water alone, or containing only a little CO_2, is so poor a solvent for soil PO_4 that it seems inadequate as an agent for estimating availability by percolation methods.

Relative solubilities. No single method of extracting PO_4 from soil, whether by equilibrium or by percolation, has been found always adequate to show whether a soil will supply phosphate to plants in sufficient amount and at a rapid enough rate to support satisfactory plant growth. But the *relative solubility* in two reagents of different power seems to give a figure which indicates very well the phosphate value for many soils. When the PO_4 found by percolation with 0.001 *N* HCl is 60 per cent or more of the amount found by percolation with 0.05 *N* HCl, the soil will supply plant growth adequately, provided the total found by 0.001 *N* HCl is 300 p.p.m. or more. When the PO_4 extracted by the more dilute acid is less than 50 per cent of the amount dissolved by the 0.05 *N* acid the soil is likely to be deficient in supporting plant growth even though the total amount found by the 0.05 *N* acid is adequate, provided it were available. The greater the difference in the amounts extracted by the two different concentrations of acid, the more likely is the soil to be deficient in supplying phosphate.

In general, more of the PO_4 in soils is contained in the fine than in the coarse particles, and the finer the particles the more available the PO_4 will be to plants. But when the percentage of clay and silt in soils was multiplied by the number of parts per million of PO_4 found in the soil, the figures did not always properly represent the PO_4 supplying power of the soil.

PO_4 dissolved from soil by an acid increases as the pH of the soil decreases and as the ratio of solvent to soil increases.

In making equilibrium extracts 1 per cent of a number of common salts added to the water did not much change the amount of PO_4 dissolved. Salts of iron and copper greatly decreased the PO_4 dissolved.

The method proposed by von Wrangell appears very promising so far as the writer has been able to test it, which is very little.

The methods proposed by Arrhenius, extraction with 1 per cent NaCl in 0.002 *N* H_2SO_4; by Dirks and Scheffer, extraction with CO_2 and $CaCO_3$; by Christensen's Azotobacter method; by Dyer's 1 per cent citric acid extract; by Fraps' 0.2 *N* HNO_3 method; by water extracts with varied proportions of soil to water; and by Lemmerman's "relative solubility" method; have been examined and none of them found generally successful with all kinds of unknown soils, though all of them may give quite useful information when applied to the kind of soil for which they were designed.

Successive water extracts made by the method of diffusion with collodion bags give a much better indication of the continuous supplying power of the soil than do single equilibrium extracts but do not with certainty give proper relative values to all soils.

REFERENCES

(1) AMES, J. W., AND GERDEL, R. W. 1927 Potassium content of plants as an indicator of available supply in soil. *Soil Sci.* 23: 199–216.

(2) ARRHENIUS, O. 1929 The phosphoric acid question in the cultivation of sugar cane in Java. *Chem. Abs.* 23: 2780.

(3) BLANCK, E. 1926 A contribution to the determination of the soil's need for fertilizer. *Ztschr. Pflanzenernähr. Düngung. u. Bodenk.* (B) 5: 118; also *Jour. Landw.* (1928). 75: 343–52.

(4) BURD, J. S., AND MARTIN, J. C. 1923 Water displacement of soils and the soil solution. *Jour. Agr. Sci.* 13: 265–295.

(5) CHRISTENSEN, HARALD 1915 Studies on the influence of soil conditions on bacterial life. *Centbl. Bakt.* 43 (II): 1–166.

(6) DAS, S. 1926 Determination of PO_4 in calcareous soils. *Chem. Abs.* 20: 2038.

(7) DIRKS, B., AND SCHEFFER, F. 1928 Rapid methods for the determination of the phosphorus requirements of soils. *Landw. Jahrb.* 67: 779.

(8) DYER, BERNARD. 1894 Analytical estimation of probably available mineral plant food in soils. *Trans. Chem. Soc.* 65: 115–167.

(9) ENGELS, O. 1926 Comparison of the methods of Neubauer and Lemmermann. *Ztschr. Pflanzenernähr. Düngung. u. Bodenk.* (B) 5: 537.

(10) FAILYER, G. H., SMITH, J. G., AND WADE, H. R. 1908 The mineral composition of soil particles. U. S. Dept. Agr. Bul. Soils Bul. 54.

(11) FRAPS, G. S. 1909 Active phosphoric acid and its relation to the needs of the soil for phosphoric acid in pot experiments. Texas Agr. Exp. Sta. Bul. 126.

(12) HALEY, D. E., AND HOLBEN, F. J. 1927 A biological measurement of available soil potassium. *Soil Sci.* 24:345–350.

(13) HIBBARD, P. L. 1930 An aparatus for percolation at a uniform constant rate, etc. *Indus. and Engin. Chem.* Anal. Ed. 2: 404.

(14) LEMMERMANN, O. 1923, 1926 Methods for determination of relative solubility of soil phosphate. *Ztschr. Pflanzenernähr. u. Düngung.* (A) 2: 363–70; (B) 5: 105–118.

(15) NEUBAUER, H., AND SCHNEIDER, W. 1923 Food consumption of germinating plants and their use in the determination of the fertilizer requirements of soils. *Ztschr. Pflanzenernähr. u. Düngung.* (A) 2: 329–362.

(16) NIKLAS, H., AND HOCK, A. 1927 The biochemical Azotobacter method for testing the phosphate needs of soil. *Ernähr. Pflanze.* 19: 297–300.

(17) NIKLAS, H., SCHARRER, K., AND STROBEL, A. 1926 Phosphate solubility and growth of Azotobacter. *Landw. Jahrb.* 63: 387–410.

(18) NIKLAS, H., AND HIRSCHBERGER, W. 1925 A new method for the rapid determination of the phosphoric acid requirements of our soils. *Chem. Abs.* 19: 1610.

(19) PARKER, F. W., AND FUDGE, J. F. 1927 The colorimetric determination of organic and inorganic phosphorus in soil extracts and in the soil solution. *Soil Sci.* 24: 109–117.

(20) PIERRE, W. H., AND PARKER, F. W. 1927 The use of collodion sacks in obtaining clear soil extracts for the determination of water-soluble constituents. *Soil Sci.* 23: 13–32.

(21) RUSSELL, E. J. 1921 Soil Conditions and Plant Growth, p. 120. Longmans, Green and Co. London.

(22) SIMON, R. H. 1930 Effect of phosphate and lime upon the rate curve of solubility of a Wooster silt loam soil. *Soil Sci.* 29: 71.

(23) TEAKLE, L. J. H. 1928 Phosphate in the soil solution as affected by reaction and cation concentration. *Soil Sci.* 25: 143–162.

(24) TRUOG, E. 1930 The determination of readily available phosphorus in soils. *Jour. Amer. Soc. Agron.* 22: 874.

(25) VANSTONE, E. 1925 Available phosphate in soils. *Jour. Agr. Sci.* 15: 460.

(26) WINOGRADSKY, S. 1928 Note on the Azotobacter test for available phosphate in soils. *Compt. rend. Acad. Sci. (Paris).* 187: 161–165.

(27) WRANGELL, M. VON 1926 I. Soil phosphate and need for phosphate. *Landw. Jahrb.* 63: 627–668; II. Colorimetric method for determination of PO_4. *Ibid.* 63: 669–675.

(28) WRANGELL, M. VON 1930 III. The determination of available plant nutrients in the soil. *Ibid.* 67: 149–169.

(29) WRANGELL, M. VON AND HAASE 1926 IV. Phosphate content of natural soil solution. *Ibid.* 63: 707–738.

(30) WRANGELL, M. VON AND KOCH 1926 Solubility laws as applied to tertiary phosphates. *Ibid.* 63: 677–706.

(31) WRANGELL, M. VON, AND MAYER, L. 1926 V. A study of the root soluble portions of soil phosphoric acid, a comparison of the Neubauer method with the expressed solution colorimetric method. *Ibid.* 63: 739–775.

Brief abstracts of articles I-V appeared in *Chem. Abs.* (1927) 21: 2752, 2857, 4003.

THE AVAILABILITY OF THE NITROGEN IN FARM MANURE UNDER FIELD CONDITIONS

A. FLOYD HECK

University of Wisconsin[1]

Received for publication July 14, 1930

A great deal of work has been reported on the availability of the nitrogen from farm manure. By far the greater part of this work has been conducted in the laboratory or greenhouse. A recent paper (5) from this laboratory is of this nature, and shows that little other than the liquid manure or ammonia nitrogen is available for plant growth. These results support the findings of Barthel and Bengtsson (1, 2) who report that only the ammonia nitrogen in manure is available. Reliable field data on this subject are not so plentiful. Most of the field data with farm manure are reported in acre yields from a given application of manure in tons an acre and as a rule neither the amount of nitrogen recovered in the crop nor the amount and kind of nitrogen added in the manure are reported. The Ohio (7) results are somewhat of this nature but if average composition for the crop yields are used, the results show an availability of the nitrogen in the manure varying from nothing to about 30 per cent. Figures obtained in this way are too indefinite to be of any great value. The work done at the New Jersey (6) station furnishes more data and shows that during a period of 20 years, from 13 to 21 per cent of the nitrogen in cattle manure is recovered in the crops grown after its application. This work was done during four consecutive 5-year periods and is supplemented by chemical analyses. In this work lime shows a slight detrimental effect which increases with time, but the availability of the manure nitrogen used without lime increased slightly in the later periods of the experiment. In this experiment the amount of manure used was much in excess of the amount that would ordinarily be used in general farming.

From Rothamsted, Hall (3) reports a 30 per cent utilization of manure nitrogen by mangels, which is much higher than those from the New Jersey station. Hansen (4) reports work from Aarslev (Denmark) showing a recovery of from 33 to 58 per cent of the nitrogen applied in farm manure. This work was done with carefully analyzed manure which was applied at the rate of 1/2, 1, and 1 1/2 units (1 unit equals 9,000 kgm.) per hectare. Crops were then grown in rotation and the nitrogen recovery obtained by analyses of the crops produced.

These figures, taken together, show a variation in nitrogen recovery from nothing to as much as over half of the total nitrogen in the manure. This

[1] From the department of soils.

variation is no doubt due to the variation in the quality of the manure and also to the way it was handled in its application. From previous work (5) it is logical to conclude that the value of farm manure is in direct proportion to the amount of liquid manure nitrogen which it contains when it is incorporated into the soil, and as a general rule low availability of nitrogen from farm manure means either a heavy loss of the liquid manure or ammonia nitrogen or the incorporation of excessive amounts of straw as bedding.

FIELD EXPERIMENT WITH FARM MANURE FOR SPRING BARLEY

A field study on the availability of the nitrogen in farm manure was conducted with spring barley. Fermented and fresh cattle manure and artificial manure were used. The dung and liquid manure were used alone, together, and also combined with straw as bedding. The liquid and solid portions of the manure were each obtained separately, analyzed, and then used in the proportion (by weight) of 74 per cent dung, 20 per cent urine, and 6 per cent straw. The straw was mixed grain straw cut into 1/2-inch lengths and contained 1 per cent nitrogen. The fresh manure was applied to the land immediately and either plowed down at once or allowed to dry, as the case might be. In one case it was allowed to stand in a closed container for three days and ammonify before application. The ingredients for the fermented manure were mixed together in the fresh condition and then allowed to ferment in a closed container for six weeks before application. The two artificial manures were made 18 months previously, by allowing moist grain straw to decompose, one with and the other without the application of ammonium sulfate. This manure was well rotted and contained very little other than organic nitrogen.

The plots were laid out in the field on a light sandy soil, rather low in organic matter and nitrogen. The plots were 6 by 11 feet and the manure was applied to this area at the rate of 12 tons (wet) of complete manure to the acre. Seven feet (14 rows, 6 inches apart) on one end of each plot was seeded to barley and the other 4 feet was kept clean cultivated (fallow). Two rows on the ends and 12 inches on the sides of each plot were used as border so that the harvested plot was exactly 4 by 5 feet, 20 square feet, or 10 rows 6 inches apart and each 4 feet long. The plots were grouped in two series of 7 plots each, making a rectangular tract 22 by 42 feet with the two control plots on opposite corners. The barley was planted in a solid block 14 feet wide in the middle of this tract, leaving the outside end of each plot clean cultivated for nitrate studies. All operations were carefully done by hand. Figure 1 shows the plan of these plots.

The kinds of manure used and the methods of handling the manure for the various plots are as follows:

1. Control.
2. Complete fermented manure—plowed down at once.
3. Complete fermented manure—received 1/2 inch of rain at once, was then allowed to dry before plowing down.

4. Complete fermented manure—allowed to dry before plowing.
5. Complete fremented manure—top-dressed and disked in at once.
6. Artificial manure, made without ammonium sulfate, plowed down at once.
7. Artificial manure, made with ammonium sulfate, plowed down at once.
8. Fresh manure, urine only—plowed down at once.
9. Fresh manure, dung only—plowed down at once.
10. Fresh manure, dung and urine—plowed down at once.
11. Fresh manure, dung, urine, and straw—plowed down at once.
12. Fresh manure, dung, urine, and straw—allowed to dry before plowing down.
13. Fresh manure, dung, urine, and straw, ammonified three days before application—allowed to dry before plowing down.
14. Control.

All plots received superphosphate and potassium chloride. These applications were made in such a way that the phosphorus and potassium added in

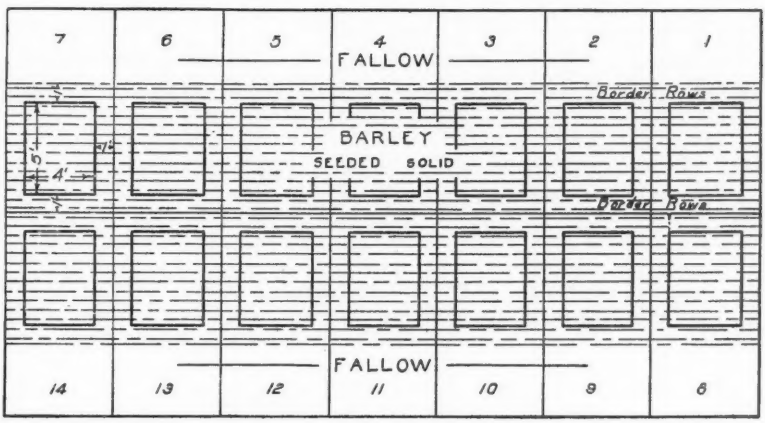


FIG. 1. PLAN OF SMALL FIELD PLOTS USED TO DETERMINE THE NITROGEN AVAILABILITY OF MANURE

the fertilizer, plus that added in the manure, would be approximately the same for all plots and this amount high enough to eliminte as much as possible the phosphorus and potassium factors. The manure was to have been applied at the rate of 12 tons an acre, but a slight error in measurement at the time of its application caused this, as well as the P and K fertilizer, to vary somewhat. These have been figured to accurate acre applications and these figures, together with the amounts of nitrogen applied per acre in the manure, are given in table 1.

The manure for plots 3, 4, 12, and 13, on which the manure was allowed to dry before plowing, was applied during the afternoon of April 22. The manure was spread evenly over the plot and allowed to dry until April 26 when the manure was applied to the other plots and all were plowed. Plot 5 was top-dressed just before seeding.

The weather conditions were not favorable for drying and loss of nitrogen, as there was only about 15 hours of fair drying weather. This was followed by two days of rain (1.15 inches) accompanied by low temperature and high relative humidity. Table 2 shows the weather conditions during this period.

The barley was seeded with a Planet Junior garden drill in rows 6 inches apart running across the plots. After the barley had come up, any vacant spaces in

TABLE 1

Applications per acre of fertilizers and manure for barley

PLOT NUMBER	SUPER-PHOSPHATE	KCl	MANURE	NITROGEN		
				Urine nitrogen	Ammonia nitrogen	Total nitrogen
	pounds	*pounds*	*tons*	*pounds*	*pounds*	*pounds*
1	355.0	266.0	.....	....	....	.....
2	98.5	98.5	11.82	....	72.5	137.1
3	97.0	97.0	11.66	....	71.4	135.1
4	95.7	95.7	11.5	....	70.4	133.2
5	94.2	94.2	11.33	....	69.3	131.2
6	93.0	93.0	11.16	....	....	136.0
7	88.0	88.0	10.56	....	....	171.1
8	264.0	88.0	0.211	61.7	....	61.7
9	93.0	186.0	8.258	....	....	59.0
10	94.2	94.2	11.33	65.3	....	125.1
11	95.7	95.7	11.5	66.4	....	141.5
12	97.0	97.0	11.6	67.25	....	143.5
13	98.5	98.5	11.82	72.6	....	151.7
14	355.0	266.0	.....	....	....	.....

TABLE 2

Weather conditions during drying of manure

	MEAN TEMPERATURE	RAIN	WIND VELOCITY	RELATIVE HUMIDITY
	°F.	*inches*	*miles an hour*	*per cent*
April 22	50	0	3.8	47
April 23	52	0	6.9	47
April 24	48	0.41	7.8	88
April 25	48	0.74	14.4	83
April 26	54	0	9.6	53

the rows longer than 3 inches were planted with sprouted barley. This procedure insured a very uniform stand, as may be seen in table 6.

The fallow ends of the plots were used for nitrate study. Beginning May 15, samples for nitrates were taken at 15-day intervals up to June 29. The samples were taken in three parts, first 6 inches, second 6 inches, and second foot, and each sample was a composite from two borings. The two borings of each sample were mixed and sifted while moist through an 8-mesh screen. A

sample of about 100 gm. was rapidly dried on the hot plate or in the oven at a temperature not to exceed 60°C. Nitrate determinations were made by the

TABLE 3

Seasonal accumulation of nitrate nitrogen under fallow on the manure plots, and also the residual nitrate nitrogen under barley at harvest

Pounds per acre 2 feet

PLOT NUMBER	NITRATE NITROGEN UNDER FALLOW				RESIDUAL NITRATE NITROGEN UNDER BARLEY AT HARVEST JUNE 29
	May 15	May 30	June 14	June 29	
1	9.2	17.5	18.0	19.0	6.8
2	15.2	68.4	103.0	138.0	7.0
3	19.8	66.4	61.0	81.0	6.25
4	17.3	61.6	47.6	65.0	6.75
5	17.6	89.0	121.0	115.0	6.25
6	6.4	9.5	14.6	23.0	6.25
7	7.0	9.0	15.0	42.7	3.75
8	81.1	70.8	69.6	70.5	....
9	8.1	11.9	12.1	21.5	....
10	32.8	41.6	28.9	149.0	....
11	17.4	51.6	52.5	79.0	....
12	24.9	29.4	37.6	60.6	....
13	22.7	20.9	42.5	67.6	....
14	9.5	13.0	18.3	34.4	....

TABLE 4

Yields, nitrogen contents, and amounts of nitrogen per acre in the barley crop

PLOT NUMBER	TOPS			ROOTS			STUBBLE		
	Weight per acre	Nitrogen content	Nitrogen per acre	Weight per acre	Nitrogen content	Nitrogen per acre	Weight per acre	Nitrogen content	Nitrogen per acre
	pounds	*per cent*	*pounds*	*pounds*	*per cent*	*pounds*	*pounds*	*per cent*	*pounds*
1	1,118	1.35	15.1	504	1.29	6.5	206	0.88	1.8
2	4,461	1.54	68.7	682	1.32	9.0	398	0.84	3.3
3	3,660	1.66	60.8	787	1.46	11.5	427	0.88	3.7
4	3,615	1.48	53.5	687	1.35	9.3	365	0.90	3.3
5	4,351	1.76	76.6	672	1.57	10.5	422	0.92	3.9
6	1,101	1.60	17.6	345	1.38	4.7	120	1.05	1.26
7	1,124	1.56	17.5	360	1.46	5.3	157	0.92	1.4
8	3,418	1.45	49.5	850	1.43	12.2	379	0.93	3.5
9	822	1.48	12.2	504	1.38	6.9	115	0.97	1.1
10	3,926	1.81	71.0	1,148	1.37	15.7	485	0.92	4.5
11	3,642	1.66	60.5	874	1.37	12.1	374	0.91	3.4
12	3,082	1.71	52.7	932	1.47	13.7	307	0.92	2.8
13	2,479	1.49	36.9	759	1.35	10.2	360	0.96	3.5
14	943	1.61	15.2	437	1.25	5.5	157	1.01	1.5

phenol-di-sulfonic acid method, alum and saturated lime-water being used as the flocculating agents. The nitrate nitrogen was calculated in pounds per

acre 2 feet, based on 4,000,000 pounds per acre foot. The determinations seldom showed more than 6 pounds of nitrate nitrogen in the second foot,

TABLE 5

Nitrogen applied in manure and that recovered from it by the barley crop

PLOT NUMBER	NITROGEN APPLIED IN MANURE			TOTAL NITROGEN IN BARLEY CROP	NITROGEN RECOVERED FROM MANURES	
	Urine nitrogen	Ammonia nitrogen	Total nitrogen		Of urine or NH_3-N	Of total nitrogen
	pounds per acre	*pounds per acre*	*pounds per acre*	*pounds per acre*	*per cent*	*per cent*
1	.....	....	.....	23.4	....	....
2	.....	72.5	137.1	81.0	80.2	42.4
3	.....	71.4	135.1	76.0	74.6	39.4
4	.....	70.4	133.2	66.1	61.5	32.5
5	.....	69.3	131.2	91.0	98.5	52.0
6	.....	....	136.0	23.6	....	0.6
7	.....	....	171.1	24.2	....	0.8
8	61.75	....	61.75	65.2	68.7	68.7
9	.....	....	59.0	20.2	....	....
10	65.3	....	125.1	91.2	104.7	54.7
11	66.4	....	141.5	76.0	80.2	37.6
12	67.25	....	143.5	69.2	69.0	32.3
13	72.6	....	151.7	50.6	38.0	17.7
14	.....	....	.....	22.2	....	....

TABLE 6

The effect of manure on the tillering of barley

PLOT NUMBER	PLANTS PER SQUARE FOOT	TILLERS	
		Per square foot	Per plant
1	16	24.0	1.5
2	13.5	44.5	3.3
3	16.5	48.0	2.9
4	15.5	40.5	2.6
5	16.5	60.0	3.6
6	13.5	19.0	1.4
7	15.5	21.5	1.4
8	12.5	42.5	3.4
9	12.0	17.0	1.4
10	17.5	52.0	3.0
11	14.5	43.0	3.0
12	15.0	41.0	2.7
13	16.5	41.0	2.5
14	13.5	17.0	1.3

indicating that there was practically no leaching of nitrate during the experiment. One possible exception to this was plot 8, where the urine alone was used. In this case 13.6 pounds of nitrate nitrogen was found in the second foot

at the first sampling, which seemed to indicate leaching of the nitrogen in the urea stage. Table 3 gives the nitrate nitrogen in pounds per acre, 2 feet, at the various sampling dates.

The barley was harvested on June 29. At this time it was fully headed. The crop from the entire plot (20 sq. ft.) was dried, weighed, ground, and sampled for nitrogen determination. The soil from two rows of barley each 2 feet long (2 q. ft). and 8 inches deep, was carefully removed from each plot and the roots and stubble washed out. When the roots and stubble were partially dry all foreign matter was carefully removed and the fibrous roots separated from the stubble. Both were dried, weighed and ground for analysis. The amounts of nitrogen were determined in the tops, roots, and stubble, and the proportions of the manure nitrogen recovered by the barley calculated. The number of plants to the square foot and the tillers to each plant for each plot were determined. These data are given in tables 4, 5, and 6.

DISCUSSION

The recovery of nitrogen from the manure in this work varied from nothing in case of the dung and artificial manures to over half the total or all of the ammonia or urine nitrogen in cases of the top-dressed fermented complete manure and the fresh urine-dung mixture. There are several factors which seem to influence the availability of manure nitrogen. Among these may be mentioned; the ratio of ammonia or urea nitrogen to the total, the proportion of bedding or energy material in the mixture, and the methods of handling. The last factor would include storage, whether fresh, ammonified, or completely fermented and also methods of application, whether top-dressed or plowed under, or whether allowed to dry or worked in immediately after spreading.

Table 5 shows that where the complete manure is top-dressed and disked in at once and where the dung and urine are plowed down at once, all of the ammonia or urine-nitrogen is recovered in the barley. Both complete fresh manure and complete fermented manure when plowed under at once give a recovery of 80 per cent of the soluble nitrogen. With the fermented manure, plowing down reduces the recovery 18 per cent as against top-dressing. Two factors may have operated here to give these results. The shallower incorporation places and holds the soluble nitrogen in the zone of the young plant roots so that the plant is able to obtain its nitrogen earlier. The top-dressed plot showed this to a marked degree from the earliest growth period. In the second place, the shallower incorporation is more conducive to nitrification earlier in the season because of the higher temperature and better aeration. This is shown by the nitrate curves in figure 2. The nitrate curve for the top-dressed manure is from 2 to 5 days ahead of the curve for the plot where the manure is plowed down at once, and this condition was reflected in the crop from the early seedling stage. The addition of fresh straw gives even a greater depression than plowing down the fermented manure. This depression is caused by the growth of soil microorganisms as a result of the increased amount

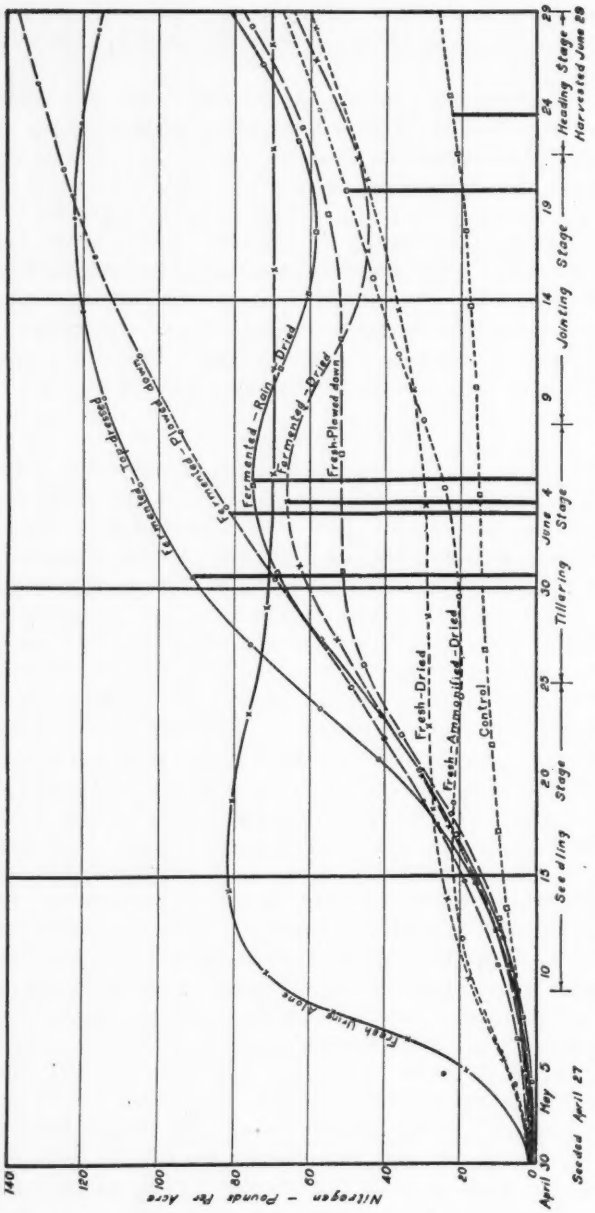


FIG. 2. NITRIFICATION CURVES ON FALLOW DURING THE GROWTH PERIOD OF SPRING BARLEY ON SIMILARLY MANURED LAND

(The heavy vertical lines represent the earliest date during the growing period when the amount of nitrate nitrogen in the fallow equals the total nitrogen in the crop at harvest time.)

of readily available energy material. This biological activity brings about a slowing up of nitrate accumulation during the tillering and early jointing stages.

The depression in nitrogen recovery, caused by the drying of the manure after spreading in the field, is probably due to the volatilization of ammonia nitrogen, and the amount of the depression depends upon the previous handling of the manure and the amount of drying to which it is exposed. In case of the fermented manure, 1½ days' drying depresses the recovery 19 per cent, but when this manure is spread immediately before a ½-inch rain, the depression is only about one-third of this amount. The depression from the drying of fresh manure is only about one-half that of the fermented manure. In the case of the fresh manure, the nitrogen is in the form of urea with less chance of loss by volatilization. The depression in case of the fresh manure is no doubt due to the loss of ammonia formed during the drying process. Where the fresh manure is allowed to stand for three days and ammonify and is then subjected to drying for 1½ days after being spread, only about 38 per cent of the nitrogen in the liquid manure is recovered in the crop. The greater loss in case of the freshly ammonified manure in comparison with the fermented manure is accounted for by the fact that the nitrogen in the former is largely in the form of ammonium carbonate, whereas in the latter case, part of the nitrogen is held as the ammonium salts of volatile organic acids such as acetic and butyric. As the salts of these acids, the ammonia is less volatile than as the carbonate and hence the loss is slower in the fermented than in the freshly ammonified manure.

There is practically no recovery of the nitrogen in the artificial manures, although they contained as much nitrogen or more than the animal manures and were in a well-rotted condition. The fresh dung, even when used alone, gives a depression below the controls. Practically all of the nitrogen in these manures is in the organic form and they also contain enough carbonaceous energy material to depress the recovery of any available nitrogen that may be present. This is particulally true of the dung. It is rather strange to note that the nitrogen from the liquid manure, when used alone, is recovered only to the extent of 68 per cent, but when used in conjunction with dung, which gives a depression, the recovery is raised to 104 per cent of the liquid manure nitrogen. This apparent discrepancy may be explained by leaching. Nitrate determinations on the liquid manure plot indicate that there is considerable leaching of the urea nitrogen apparently before it has a chance to change to ammonia. In this particular case at a very early date a large quantity of nitrate nitrogen was found in the second foot. When the liquid manure is used in conjunction with dung it is held more or less mechanically in the surface soil so that the plant is able to utilize more of the nitrogen at an early date.

Nitrate relations. A study of the nitrate curves in figure 2 in relation to crop growth and the availability of manure nitrogen is very interesting. The four plots on which fermented manure was used fall into two pairs, according to the nitrate curves, the two which were allowed to dry after spreading and

the two worked into the soil at once. Of the two worked in at once, the top-dressed plot is the higher in the seedling and tillering stages. Plowing down slows up the nitrification rate during these stages of growth and causes a

TABLE 7

Rainfall for April, May, and June, 1929, at Madison, Wisconsin

DAY	APRIL	MAY	JUNE
	inches	*inches*	*inches*
1	0.31	T	0
2	T	0	0
3	0	0	0
4	0.01	0	0
5	0.02	0	T
6	1.09	0	0
7	T	0	T
8	0	0.02	0
9	0	0	0
10	0.27	0.44	0
11	0.45	0.17	0.34
12	T	0	T
13	0	0	0.36
14	0	0.11	0.03
15	0	0.05	0
16	T	0	1.97
17	T	0.06	T
18	0	T	0.98
19	0.20	0	0.05
20	0.03	0	0
21	0	0	0
22	0	T	T
23	0	0.35	T
24	0.41	0	0.05
25	0.74	0	0.07
26	0	0.03	0.04
27	0.53	0.05	0.45
28	0.02	0	0
29	0.10	0.03	0
30	0.11	0	0.01
31		0	

T = Trace.

lesser amount to be recovered by the barley, although the nitrate nitrogen on this plot is higher at a later date. The nitrates for the two plots where the manure is dried are again parallel, with the one which received rain always

higher and at the same time giving the greater recovery. This is because of the lesser loss of nitrogen on drying after the rain. The shape of these curves is significant. The rise during the seedling and tillering stages is slower than where the manure is worked in without drying. The drop coming during the late tillering and early jointing stages may be caused by the growth of higher soil fungi which seem to show up at about this time. During this period these organisms are using the energy material of a cellulose nature in the manure and at the same time using the nitrogen more rapidly than nitrification is going on. Later in the season the nitrate curves on these two plots take an upward trend after the rains of June 16 and 18. Better conditions for nitrification, due to moisture, coming perhaps on the downward growth curve of the higher soil fungi, may be responsible for this upward trend, but coming so late in the life of the plant, it is of little benefit. The effect of the growth of the higher soil fungi may be seen in the top-dressed plot. During the last two weeks, fruiting bodies of *Stropharia semiglobota* and a species of *Nectria* apleared in abundance and at the same time there was a downward trend in the nitrate curve.

In each of these four plots the earliest point in the nitrate curve where the amount of nitrate nitrogen corresponds to the amount of nitrogen recovered by the barley, falls some place during the tillering period. It seems also that the earlier this comes, the greater the amount of nitrogen is recovered in the crop. On the control and plot 13 (ammonified and dried) the nitrate curves are low during the seedling and tillering stages and this point comes late in the jointing stage with a low recovery of the nitrogen applied. On the other hand, fresh urine alone gives a high nitrate curve early in the seedling stage of the plant, with a low percentage recovery, partially due perhaps to leaching of urea-nitrogen and partially to the bulk of the nitrates coming too early in the period of plant growth. From these data it appears that there is a relation between the shape of the nitrate curve and the growth of plants and their utilization of nitrogen. If the rise comes too early or before the late seedling and tillering stage, there is a tendency for leaching losses to take place. If, on the other hand, the nitrate curve rises slowly and is low during the seedling and tillering stages, the plant passes its stage of most active nitrogen assimilation and the result is a low yield and a low nitrogen assimilation. A nitrate curve similar to that of plot 5 seems to be the one most conducive to maximum nitrogen assimilation and to maximum plant growth, and this curve perhaps approached more nearly the growth curve of the plant than any of the others. It would follow then that the nitrate curve which most nearly conforms to the growth curve of the plant during its early stages, both in regard to time and amount of nitrate accumulation, is the one which is the most likely to produce the maximum plant growth. From a practical standpoint the curves in figure 2 show that manure should be plowed under a week or two earlier than it is top-dressed and for the best results the liquid manure should be applied after the crop is up.

The kind and amount of the material used as bedding are important fac-

tors in the availability of manure nitrogen. Table 5 shows that the addition of 6 per cent by weight of straw to the liquid and solid manure mixture reduces the availability of the liquid manure nitrogen over 20 per cent. Wood shavings used as an absorbent are even more detrimental than straw. The depressing effect of these substances is due to the use of ammonia and nitrate nitrogen by soil fungi, which at the same time use certain carbonaceous materials in the straw or shavings as energy for their growth. Niemeyer (8) has shown that the use of peat as an absorbent has two distinct advantages over straw or shavings: First, it is a better absorbent and more of the liquid manure is saved and applied to the field, and, second, there is very little energy material in the peat for the growth of soil fungi and as a result the depressing effect from this source is largely eliminated.

It is very possible that the percentage recoveries reported in this paper will hold true only for manures of a similar ratio of soluble to insoluble nitrogen. It is also very likely that a given amount of energy material of a cellulose nature will use a given amount of soluble nitrogen and not a percentage of the amount present. In cases of low water-soluble or ammonia nitrogen it is just possible that all of it may be used by the soil microörganisms and none recovered by the plant.

SUMMARY

A field study of the availability of the nitrogen in cattle manure was made with spring barley and the following points seem to be outstanding:

The amount of nitrogen recovered in the barley crop was never greater than the amount of ammonia or liquid manure nitrogen applied. The results indicate that only the ammonia or liquid manure nitrogen is available for the first crop after the manure is applied to the soil. Little if any of the water-insoluble nitrogen in the manure is recovered in the first crop.

When liquid manure is applied alone before the crop is seeded, the recovery is less than when applied in conjunction with the dung. This difference seems to be due in part to leaching of the urea before its change to ammonia. If liquid manure is to be used alone it is perhaps best applied to the growing crop and worked into the soil at once.

Complete manure turned under immediately on spreading gives a recovery of 80 per cent of the urea or ammonia nitrogen which it contains. There is no difference in the availability of nitrogen between the manure fermented in storage and the fresh manure when they are turned under immediately on spreading.

Top-dressing gives a higher availability than plowing down. The nitrification of manure top-dressed and disked in is more rapid than when it is plowed under.

Measured in terms of non-recovery, the greatest loss of nitrogen in spreading manure and allowing it to dry or partially dry before being plowed under, occurs with manure which has ammonified but not fermented. The next greatest loss is from the completely fermented manure. The fresh manure gives a still smaller loss under these conditions, and where the fermented manure is spread just previous to a rain the loss from drying is not more than a few per cent. The better the conditions for drying and the greater the proportion of the nitrogen in the form of ammonium carbonate, the greater the loss of nitrogen in handling, spreading, and subsequent drying.

The addition of straw to manure decreases the amount of nitrogen recovered in the first crop. Six per cent of straw used as bedding in the manure reduced the recovery more than 20 per cent.

Conditions which give a nitrification curve most similar to the growth curve of the plant and furnish sufficient nitrogen for rapid growth during the seedling and tillering stages, are most conducive to high yields and the greatest recovery of manure nitrogen.

REFERENCES

(1) BARTHEL, C., AND BENGTSSON, N. 1924 Bidrag till frågan om stallgödselkvävets nitrifikation i åkerjorden. IV. Meddel. Centralanst. Försöksv. Jordbruksområdet. (Sweden) 269.

(2) BARTHEL, C., AND BENGTSSON, N. 1926 Bidrag till frågan om stallgödselkvävets nitrifikation i åkerjorden. V. Meddel. Centralanst. Försöksv. Jordbruksområdet. (Sweden) 311.

(3) HALL, A. D. 1917 The Book of the Rothamsted Experiments. New York.

(4) HANSEN, N. A. 1928 Gødningsforsøg paa Forsøgsstationen ved Aarslev 1911–1926. *Tidsskr. Planteavl.* 34: 373–523.

(5) HECK, A. F. 1931 Conservation and availability of the nitrogen in farm manure. *Soil Sci.* 31: 335–363.

(6) LIPMAN, J. G., A. W., AND PRINCE, A. L. 1928 Field experiments on the availability of nitrogenous fertilizers, 1923–1927. *Soil Sci.* 26: 1–25.

(7) Maintenance of soil fertility, The 1924 Ohio Agr. Exp. Sta. Bul. 381.

(8) NIEMEYER, P. 1929 Zersetzung und Wirkung von Stroh- und Torfstreustalldünger im Boden. *Landw. Vers. Sta.* 108: 305–348.

PLATE 1

Barley Growth as Affected by Various Fertilizer Treatments

Fig. 1. Barley on the control, no manure or nitrogen added.

Fig. 2. Barley from 12 tons an acre of artificial manure made from straw by the use of ammonium sulfate, and plowed down immediately after being spread.

Fig. 3. Barley from 12 tons an acre of complete fermented manure, plowed down immediately after being spread.

Fig. 4. Barley from 12 tons an acre of complete fermented manure,—allowed to dry in the field before being plowed down

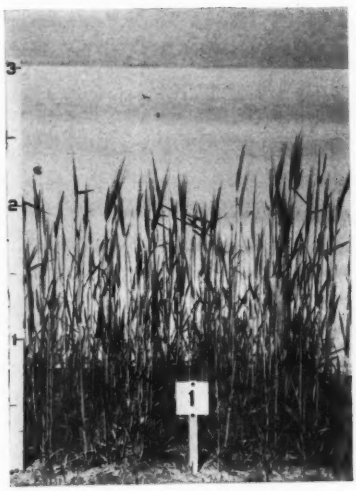


FIG. 1

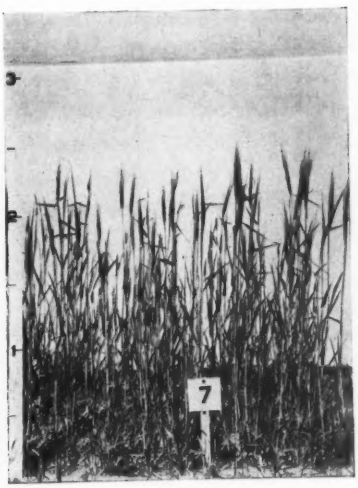


FIG. 2

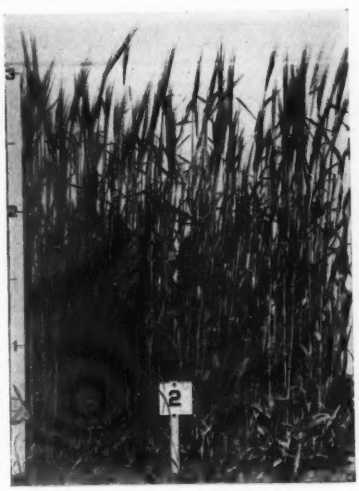


FIG. 3

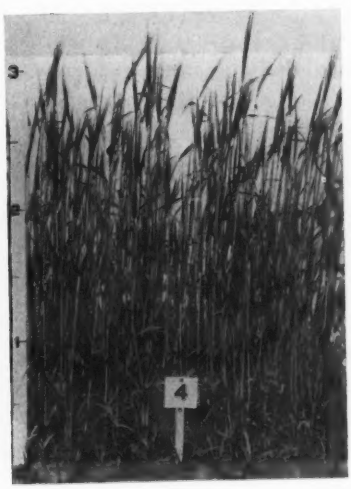


FIG. 4

DETERMINATION OF SOIL ORGANIC MATTER

C. J. SCHOLLENBERGER

Ohio Agricultural Experiment Station

Received for publication December 29, 1930

Several years ago, the writer described a simple procedure for the approximate determination of soil organic matter (5), based upon the oxidation of the sample by heating with concentrated sulfuric acid containing excess chromic acid at such a rate that the temperature reaches 175° C. in 90 seconds, cooling at once, diluting and titrating the chromic acid not consumed in oxidizing organic matter by a standard solution of ferrous ammonium sulfate with diphenylamine as internal indicator. Although no great degree of precision was claimed for this method, it seems to have found considerable favor, judging from the number of investigators who have reported results obtained by its use. Degtjareff (1) reports a study of the method, substantially as originally described except that more care was taken to have the time and temperature uniform for all tests, by heating in a sulfuric acid bath at 165° C. for 10 minutes. He also advises close attention to the color change at the endpoint. His results as reported show that the method is capable of considerable accuracy, and for many purposes the indications obtained in this way should be quite as satisfactory as those by procedures for which great precision is claimed. In the same paper, an alternate procedure is described which differs principally from the original method by the inclusion of hydrogen peroxide in the oxidizing mixture and the omission of heating. As in the first method, the excess of oxidizing agent is titrated with standard ferrous ammonium sulfate and diphenylamine is employed as internal indicator.

A paper presenting the results of a very complete study of the indicator properties of diphenylamine by Kolthoff and Sarver (3) has appeared recently. The data obtained and conclusions drawn from a study of the same indicator in ferrous iron-dichromate titrations have been published (6). The author's experience has been in agreement with the conclusions of Kolthoff and Sarver that diphenylamine, or rather its oxidation product, is a true oxidation-reduction indicator developing a characteristic blue color at a potential of about 0.51 volt as measured by a standard set-up for electrometric titrations including a saturated potassium chloride-calomel electrode, at about 25°C. In the usual titration of a ferrous salt by dichromate, the oxidation-reduction potential is buffered by the mixture of ferrous and ferric ions and the potential mentioned is reached at a comparatively flat portion of the titration curve; the diphenylamine color therefore appears prior to complete oxidation of iron and

increases in intensity as the titration is completed. On back-titration with titanous chloride, the color fades gradually until the potential has fallen to that point, when it disappears entirely. In back-titration of excess chromic acid with ferrous salt solution, however, the potential drop after complete reduction of chromic acid is very gradual, since Fe'' cannot reduce Fe''', and a considerable excess of ferrous salt is necessary to take the potential below the point at which the indicator still shows color. Under these circumstances, the endpoint is not sharp, being indicated by a pronounced fading rather than a total disappearance of blue, as was noted when the procedure was first described (5).

The author has found that by the addition of either phosphoric or hydrofluoric acid, Fe''' is inactivated by formation of slightly dissociated salts, the buffer effect greatly diminished, and the potential consequently lowered. At the point of complete oxidation of iron or reduction of excess chromic acid the titration curve is asymptotic, and an extremely small increment of the titrating solution is sufficient to take the oxidation-reduction potential past the critical value for color change. The endpoint is then very sharp and easily seen, since another effect of the inactivation of Fe''' is the bleaching of the normal yellow color. Knop (2) states that the presence of sufficient phosphoric acid to destroy the yellow color of ferric salt is advantageous, but gave no other explanation for its action. The author did not use it, as results seemed sufficiently exact without it. Also, it has been his custom to determine available phosphoric acid in soils by the very sensitive ceruleomolybdate method at the same time that the test for organic matter was made, and the use of phosphoric acid in one determination is undesirable since it may lead to error from contamination of the other. Hydrofluoric acid is of course without this objection, but is unpleasant and even dangerous to handle. Szebellédy (7) states that the diphenylamine endpoint is more satisfactory in the presence of ammonium fluoride, but there seems to be no reason why sodium fluoride should not serve as well. Lang and Kurtz (4) found sodium fluoride a desirable addition in a somewhat similar titration, but state the use of potassium fluoride was not satisfactory as it seemed to interfere with color development. The author has tried only hydrofluoric acid and sodium fluoride, and prefers the latter. All fluorides are of course destructive to glassware, but the error introduced by solution of Pyrex glass during the brief time necessary for titration is of no practical consequence, being very small and compensated by the blank determination.

Besides the lack of sharpness in the diphenylamine endpoint, which can be overcome by addition of phosphoric or hydrofluoric acid, the indicator has several other peculiarities which have caused some to condemn it after brief experience. The most disconcerting of these is the occasional failure to develop the blue color when added to a solution containing excess chromic acid; in such cases it is always noticed that on addition of the first drop of ferrous sulfate the color appears, and increases as the next two or three drops are added. The explanation for this puzzling behavior is that not diphenylamine itself, but a product of its partial oxidation, is the indicator, as Kolthoff and Sarver

(3) have pointed out. Like many other organic substances, diphenylamine is not very readily oxidized by chromic acid alone in cold dilute acid solution, but if a trace of substance readily oxidized is added, "induced oxidation" of the more resistant substance takes place. Other instances of the same phenomenon and theories explaining it are given by Lang and Kurtz (4). Another objectionable feature is the appearance of a green oxidation product instead of the blue indicator substance. This is especially likely to happen when diphenylamine is added to a solution containing excess chromic acid. In these respects also, the trouble is much reduced by addition of phosphoric or hydrofluoric acid, and by limiting the amount of diphenylamine added to the solution. Two or three drops of a one-half per cent solution is ample for the production of an intense endpoint in a 200-cc. volume, and more is undesirable.

Extended experience in the determination of organic matter by the chromic acid oxidation method under discussion has indicated that it is not at all necessary to prepare the solution of dichromate in concentrated sulfuric acid as originally specified, although it is desirable to do this if many determinations are to be made at the same time. Very good results are obtained by weighing out the proper amount of pure potassium dichromate, previously pulverized and dried, transferring it to the test tube, adding the sample, and finally washing down the walls of the tube with 10 cc. pure sulfuric acid, and heating at once. This is a useful expedient in the examination of samples high in organic matter, as the usual 0.5-gm. sample may be used with sufficient oxidizing agent and only the usual amount of acid. By this procedure also, one is able to determine both the blank and titer of a partially deteriorated ferrous ammonium sulfate solution, still of sufficient strength to be usable. In this case, potassium dichromate is the primary standard; it is well adapted to the purpose, as it is easily obtained in pure form, is anhydrous and non-hygroscopic. The equivalent of 1 cc. 0.2 *N* solution is 0.009807 gm., equal to 0.0006 gm. carbon or approximately 0.0012 gm. organic matter. For the determination of organic matter in a 0.5-gm. sample of average soil, the equivalent of 20 cc. 0.2 *N* solution, 0.1961 gm. $K_2Cr_2O_7$ may be used. The weight of the salt taken may be varied as required, within reasonable limits.

It is recommended, therefore, that the procedure for determination of organic matter in soil originally described be amended as follows: Proceed as originally directed, or according to the modification suggested in the last paragraph, or one of the procedures described by Degtjareff (1), up to the point at which the solution is transferred to a beaker for titration. Dilute with recently boiled and cooled water, to at least 10 but not more than 15 times the volume of concentrated sulfuric acid present, and cool. To this solution add, in volume equal to half that of concentrated sulfuric acid in the solution, either 85 per cent phosphoric acid or 48 per cent hydrofluoric acid or the approximate equivalent of the latter in powdered sodium fluoride, i.e., 5 gm. NaF for 10 cc. concentrated sulfuric acid. Add two or three drops of diphenylamine indicator solution and titrate with standard ferrous ammonium sulfate solution to total disappear-

ance of blue from the green solution. Deduct the burette reading from that of a blank titration conducted under precisely similar conditions except that no sample is used, and from the number of cubic centimeters of iron solution equivalent to organic matter in the sample calculate the amount present. One cubic centimeter 0.2 *N* ferrous ammonium sulfate solution is equivalent to approximately 0.25 per cent organic matter in a 0.5-gm. sample, or 2.5 tons in an acre.

REFERENCES

(1) DEGTJAREFF, W. TH. 1930 Determining soil organic matter by means of hydrogen peroxide and chromic acid. *Soil Sci.* 29: 239–245.

(2) KNOP, J. 1924. Diphenylamine as indicator in the titration of iron with dichromate solution. *Jour. Amer. Chem. Soc.* 46: 263–269.

(3) KOLTHOFF, I. M., AND SARVER, L. A. 1930. Properties of diphenylamine and diphenylbenzidine as oxidation-reduction indicators. *Jour. Amer. Chem. Soc.* 52: 4179–4191.

(4) LANG, R., AND KURTZ, F. 1929. Maszanalytische Bestimmung von Mangan als Manganisalz nach einem neuen Verfahren. *Ztschr. Anorgan. Allg. Chem.* 181: 111–120.

(5) SCHOLLENBERGER, C. J. 1927 A rapid approximate method for determining soil organic matter. *Soil Sci.* 24: 65–68.

(6) SCHOLLENBERGER, C. J. 1931 Diphenylamine as indicator in the determination of iron in silicates. *Jour. Amer. Chem. Soc.* 53: 88–98.

(7) SZEBELLÉDY, L. 1930 Über die Bestimmung des Eisens mit Kaliumdichromat. *Ztschr. Anal. Chem.* 81: 97–103.

THE MODELING OF SOILS, AN AID IN THEIR STUDY

R. H. CARR[1]

Purdue University

Received for publication September 15, 1930

Many students of soils who have had extensive training in some of the more advanced lines, such as classification, hydrogen-ion determination, base exchange and colloidal characteristics, have been found very deficient in the ability to rate soils in the fields, either for their own benefit or for that of farmers, appraisers, or loan companies. This is believed to be partly because they have forgotten most of what they learned in the days when they made mud pies, dogs, and fences out of "dirt" and also because in later years they have been afraid of getting their hands dirty with mud or probably they have thought it useless to attempt to study a soil by its "feel."

Soil, from a technical standpoint, is a complex combination of compounds and it is difficult to rate many soils properly even with the help of refined instruments. There are certain characteristics of an elementary nature, however, the knowledge of which can be readily acquired by practice, although comparatively few people have succeeded in mastering field judging.

The writer was agreeably surprised some time ago at the thoroughness with which a certain farmer who had had little "book learning" had developed by practice when plowing and while the team was resting, the ability to detect differences in the texture, structure, color, and plasticity of the soils in various places and also to tell their influence on the tilth, water-holding capacity, and fertility of a certain rented farm. He had platted the locations of the changes in surface and subsoil conditions over the 110 acres. He would estimate the organic matter and test the "feel" to find sand particles by their grittyness and count the stones in each handful of soil. He estimated the silt by its floury feel, when dry and also noted that clayey material is rough and harsh when dry, and sticky and capable of being modeled when it is wet. He took much interest in making such molds as his fancy might suggest. The interest and enthusiasm in field studies of this tiller of the soil have been somewhat contagious and the writer has had some of the students interested in soils trying their skill in rating known and unknown soils. They, too have caught the spirit and have developed enough interest to make some very creditable molds. Several of them are shown in plate 1. The students soon found that some soils are too sandy or too grainy to stick together well, or if they stick together at first they will fall apart when dry. Some that did stay together were often too fri-

[1] Professor of Agricultural Chemistry.

able to outline any distinctive facial features. Plate I shows that in the center model, the soil particles are large enough to be apparent to the eye, whereas in the largest one the soil grains are very fine. The mold is smooth and hard now, but was very plastic when wet. In the smallest model there are fairly equal amounts of sand and clay; it was made from a well-recognized loam soil which neither molds well nor has a smooth finish.

There is a growing need and desire on the part of those interested in land to learn the field characteristics of soils and their meaning in terms of "good," "medium," and "poor," so that it may be possible to predict how the soil will stand a drought such as was experienced last year or how well it will drain off the excess water which was so serious a question two years ago. If the farmer has this information he will be able to prepare early for his spring crops.

Mechanical analyses of soils are necessary for the more detailed study of soil properties, but they are tedious to carry out (except by the hydrometer method). Hence, they are not much help to the man who does the plowing and who is financially concerned with drought and excess rainfall on the piece of land he has rented for the year. It has been found possible in a few cases by practice with a quart or more of soil from each of about two dozen samples, to develop considerable skill in detecting shades of differences in sand, silt, and clay. This requires no more practice than is needed to pitch a good game of horse shoes.

PLATE 1

MODELS MADE FROM SOILS

Left—from Miami surface soil; center—from Bainbridge subsoil; right—from surface soil of Clermont type. Photo by Dr. E. J. Kohl.

MODELING OF SOILS

R. H. CARR

PLATE 1

AUTHOR INDEX

Bartholomew, R. P. Changes in the availability of phosphorus in irrigated rice soils, 209–218.

Baver, L. D., and Scarseth, G. D. The nature of soil acidity as affected by the SiO_2-sesquioxide ratio, 159–173.

Blair, G. W. Scott. The conception of flow-plasticity as applied to soils, 291–298.

Blanck, E. Handbuch der Bodenlehre, v. 2 (book review), 81.

Blaney, H. F., and Taylor, C. A. Soil sampling with a compressed air unit, 1–3.

Blaney, J. Eric, and Smith, John B. Sampling market-garden soils for nitrates, 281–290.

Bodman, G. B., and Perry, Esther P. The interrelationships of certain single-valued soil properties, 365–378.

Brown, P. E. *See* **Thompson, L. G.,** Smith, F. B., and.

Brown, S. M. *See* **Kelley, W. P.,** Dore, W. H., and.

Carr, R. H. The modeling of soils, an aid in their study, 487–490.

Clark, Norman Ashwell, and Roller, Emery M. The stimulation of Lemna major by organic matter under sterile and non-sterile conditions, 299–309.

Dhar, N. R. *See* **Rao, G. Gopal.**

Dore, W. H. *See* **Kelley, W. P.,** and Brown, S. M.

Eaton, Frank M. A large sand culture apparatus, 235–241.

Elliott, Charlotte. Manual of Bacterial Plant Pathogens (book review), 80.

Emmert, E. M. A method of oxidizing and dissolving soil for the determination of total and filtrable manganese and phosphorus, 175–182.

Fuller, James, E., and Rettger, Leo F. The influence of combined nitrogen on growth and nitrogen fixation by Azotobacter, 219–234.

Gilbert, Basil E., and Pember, Frederick R. Further evidence concerning the toxic action of aluminum in connection with plant growth, 267–273.

Greaves, J. Dudley. A mathematical study of the decrease of crop yields, 115–122.

Heck, A. Floyd. Conservation and availability of the nitrogen in farm manure, 335–363; the availability of the nitrogen in farm manure under field conditions, 467–481.

Hibbard, P. L. Chemical methods for estimating the availability of soil phosphate, 437–466.

Honcamp, F. Ergebnisse der Agrikulturchemie, v. 1 (book review), 82–83.

Hulbert, Arthur Butler. Soil (book review), 83.

Jenny, Hans. Soil organic matter-temperature relationship in the Eastern United States, 247–252.

Jensen, H. L. The fungus flora of the soil, 123–158.

Kelley, W. P., Dore, W. H., and Brown, S. M. The nature of the base-exchange material of bentonite, soils, zeolites, as revealed by chemical investigation and X-ray analysis, 25–55.

Kreybig, L. Die Bedingungen der Wirtschaftlichkeit der Handelsdüngemittel (book review), 79.

Lilleland, Omund. *See* **McKinnon, L. R.**

Lundegårdh, Henrik. Klima und Boden in ihrer Wirkung auf des pflanzenleben (book review), 81–82.

McKinnon, L. R., and Lilleland, Omund. A method of application designed to insure proper distribution of fertilizers in field trials with fruit trees, 407–411.

Mattson, Sante. The laws of soil colloidal behavior. IV. Isoelectric precipitates, 57–77; V. Ion adsorption and exchange, 311–331.

Mohr, E. C. J. Tropical Soil Forming Processes and the Development of Tropical Soils (book review), 243.

Palmer, Harold S. Soil forming processes in the Hawaiian Islands from the chemical and mineralogical points of view, 253–265.

Pember, Frederick R. *See* **Gilbert, Basil E.**

Perry, Esther P. *See* **Bodman, G. B.**

Pierre, W. H. Hydrogen-ion concentration, aluminum concentration in the soil solution, and percentage base saturation as factors affecting plant growth on acid soils, 183–207.

Pierre, W. H., and Scarseth, G. D. Determination of the percentage base saturation of soils and its value in different soils at definite pH values, 99–114.

Piland, J. R. *See* **Willis, L. G.**

Pohlman, George Gordon. Changes produced in nitrogenous compounds by Rhizobium meliloti and Rhizobium japonicum, 385–406.

Puri, Amar Nath. Interaction between ammonia and soils, as a new method of characterizing soil colloids, 93–97; a simple method of estimating total exchangeable bases in soils, 275–279.

Rao, G. Gopal, and Dhar, N. R. Photosensitized oxidation of ammonia and ammonium salts and the problem of nitrification in soils, 379–384.

Rayner, M. C. Mycorrhiza (book review), 80–81.

Rettger, Leo F. *See* **Fuller, James E.**

Richter, Charles. The temperature correction in the hydrometer method of mechanical analysis of soils, 85–92.

Roller, Emery M. *See* **Clark, Norman Ashwell.**

Salter, Frederick J. The carbon-nitrogen ratio in relation to the accumulation of organic matter in soil, 413–430.

Scarseth, G. D. *See* **Baver, L. D.**

Scarseth, G. D. *See* **Pierre, W. H.**

Schollenberger, C. J. Determination of soil organic matter, 483–486.

Schucht, Friedrich. Grundzüge der Bodenkunde, 79.

Smith, F. B. *See* **Thompson, L. G.,** and Brown, P. E.

Smith, John B. *See* **Blaney, J. Eric.**

Smith, Nathan R. Felix Löhnis, 333–334.

Stebutt, Alexander. Lehrbuch der allgemeinen Bodenkunde (book review), 84.

Taylor, C. A. *See* **Blaney, H. F.**

Thomas, Stanley. Bacteriology (book review), 82.

Thompson, L. G., Smith, F. B., and Brown, P. E. Phosphorus assimilation by soil microörganisms, 431–436.

Waksman, S. A. Martinus Willem Beijerinck, 245–246.

Willcox, Oswin W. Principles of Agrobiology, or the Laws of Plant Growth in Relation to Crop Production (book review), 243–244.

Willis, L. G., and Piland, J. R. Ammonium calcium balance: A concentrated fertilizer problem, 5–23.

Actinomyces, relation to—
alfalfa decomposition, 149.
casein decomposition, 148.
cellulose decompsotion, 146.
H-ion concentration of soil, 130, 137.
Agricultural chemistry, contributions of, 82.
Agrobiology, Principles of, a book, 243.
Alanine, changes produced in, by Rhizobium, 392.
Alfalfa meal, effect on—
actinomyces, 149.
bacteria in soil, 149.
fungus flora, 149.
Aluminum—
active, in acid soils, 269.
factor in plant growth, 183.
humates of, 59.
isoelectric—
"phospho-humate" and "silico-humates," 66.
phospho-silicates, 69, 317, 318.
method of determining, 188.
oxide as photosensitizer of ammonia, 383.
silicate, exchange reactions in, 324.
toxic action of, 267–273.
Amino benzoic acid, changes produced in, by Rhizobium, 397.
Amino-n-butyric acid, changes produced in, by Rhizobium, 393.
Ammonia—
nitrogen in manure, 351.
oxidation of, 379, 381.
photosensitizers in the oxidation of, 381.
soils and, interaction between, 93.
Ammonium—
calcium balance, 5–23.
carbonate—
effect on nitrogen fixation by Azotobacter, 226.
oxidation of, 380.
chloride—
effect on nitrogen fixation by Azotobacter, 226.
oxidation of, 380.
nitrate, effect on nitrogen fixation by Azotobacter, 226.
phosphate—
effect on nitrogen fixation by Azotobacter, 226.
oxidation of, 380.
salts, oxidation of, 379.
sulfate—
changes produced in, by Rhizobium, 400.
effect on nitrogen fixation by Azotobacter, 226.
oxidation of, 380.
toxicity of, salts, 12.
Asparagine, changes produced in, by Rhizobium, 388, 398.
Aspartic acid, effect on N fixation by Azotobacter, 226.
Aspergillus, phosphorus assimilation by, 433.
Azotobacter—
ammonia nitrogen in fluid cultures of, 229.
nitrogen fixation by, as affected by combined nitrogen, 219–234.
phosphorus assimilation by, 433.
proteolytic activity of, 225.
Bacteria—
as affected by dextrose, 141.
effect on Lemna major reproduction, 305.
legume, changes produced by, in nitrogenous compounds, 385–406.
relation to—
alfalfa decomposition, 149.
casein decomposition, 148.
cellulose decomposition, 146.
H-ion concentration of soils, 130, 137.
Rhizobium meliloti and Japonicum, effect on N compounds, 385.
Bacto-peptone, effect on N fixation by Azotobacter, 226.
Barley—
experiments with manure on, 468.
nitrogen content of, 471.
Base—
anion exchange as related to, exchange, 325.
exchange upon application of potash fertilizer, 408.
saturation as factor of plant growth in acid soils, 183.

Base-exchange—*see* also Ion exchange.
as affected by—
grinding materials, 26.
heat, 41.
capacity—
and exchangeable bases, two concepts, 96.
relation to silica-sesquioxide ratio, 166.
cation, capacity of various complexes, 311.
chemical investigations, 25–55.
complex, crystalline nature of, 42.
in—
beidellite, 29.
bentonite, 25.
natrolite, 41.
scolecite, 41.
soils, 25.
stilbite, 41.
zeolites, 25, 39.
methods, reliability of, 171.
nature of, 25–55.
X-ray analysis, 25.
Bases—
exchangeable—
base-exchange capacity and, 95.
method of estimating, in soils, 275–279.
hydrogen-ion concentration and exchangeable, 99.
replaceable, increase of, due to irrigation, 217.
saturation of soils with, determination of, 99–114.
Beidellite, base-exchange in, 29.
Beijerinck, Martinus Willem, an obituary note, 245.
Bentonite—
base-exchange in, 25.
isoelectric pH of and sesquioxides, 74.
Bluegrass, C-N ratio in, 418.
Buckwheat, as affected by manure, 344.
Calcium—
ammonium balance, 5–23.
antagonism to toxicity, 16.
carbonate, effect on ammonia injury to plants, 15.
replacing power with respect to magnesium, 44.
Carbon—
dioxide, losses in fermenting manure, 354.
nitrogen ratio in—
bluegrass, 418.
cellulose, 418.
corn stover, 418.
glucose, 418.
organic matter in soils, 413–430.
ragweeds, 418.
red clover, 418.
straw, 418.
sweet clover, 418.
tobacco stems, 418.
wood-fiber, 418.
Casein—
decomposition of, 147
effect on—
actinomyces, 148.
bacteria, 148.
fungi, 148.
Cation exchange capacity of various complexes, 311.
Cellulose—
carbon-nitrogen ratio in, 418.
decomposition of, 142, 146.
effect on—
actinomyces flora, 146.
bacterial flora, 146.
fungus flora, 143.
Clay content, determination of, 366.
Clover—
red, C-N ratio in, 418.
sweet, C-N ratio in, 418.
Colloid—
amphoteric, Donnan equilibrium in, 326.
content determination by adsorption, 366.
Donnan equilibrium in an amphoteric, 326.
sesquioxide-soil system, 71.
Colloidal—
clay acids, titration curves, 162–166.
content by adsorption, 365.
laws of soil, behavior 57–77, 311–331.
Colloids—
charge on, factors involved, 59–66.
isoelectric aluminum "phospho-humate" and "silico-humates," 66.
sodium-humate, 58.
Corn—
as affected by manure, 344.
carbon-nitrogen ratio in, 418.
Cotton, toxicity of fertilizers to, seedlings, 8.
Creatinine, effect on N fixation by Azotobacter, 226.
Crop, mathematical study of the decrease of, yields, 115–122.
Culture solution, *see* Nutrient solutions.
Cysteine hydrochloride, effect on N fixation by Azotobacter, 226.

Cystine—
changes produced in, by Rhizobium, 395.
effect on N fixation by Azotobacter, 226.
Dextrose, decomposition of, in acid and limed soils, 142.
Donnan equilibrium in an amphoteric colloid, 326.
Fertilizer—
ammonium calcium balance, 5–23.
commercial, the economy of, 79.
concentrated, mixture, injurious effects of, 9.
effect on microörganisms in soils, 139.
toxicity of, 7.
Fertilizers—
for fruit trees, 407.
method of application to insure proper distribution, 407–411.
penetration of, in soils, 408.
Fungi—*see* also Molds
composition of soil flora, 128.
decomposition of various substances by, 140.
direct isolation of, 124.
number of, in soil, 129.
proteolytic power of, 150.
relation to—
alfalfa decomposition, 149.
casein decomposition, 148.
cellulose decomposition, 146.
humus content, 130.
liming, 134.
physical character of soil, 130.
soil reaction, 130, 137.
soil, flora, 123.
Glucose, C-N ratio in, 418.
Glutanic acid—
changes produced in, by Rhizobium, 394.
effect on N fixation by Azotobacter, 226.
Glycocoll—
changes produced in, by Rhizobium, 391.
effect on N fixation by Azotobacter, 226.
Guanine, effect on N fixation by Azotobacter, 226.
Hydrogen, replaceable, method of determining, 100.
Hydrogen-ion concentration—
factor in plant growth on acid soils, 183–207.
relation to—
actinomyces in soil, 130.
bacteria in soil, 130.
exchangeable bases, 99, 103, 108.
fungus flora in soil, 130.
potassium-calcium ratio in soil solution, 198.
Hydrometer—
method of mechanical analysis of soils, 85.
temperature correction in, method, 85.
Humates—
cation exchange capacity of, 330.
electrical charge of, factors involved, 61.
isoelectric, of Al and Fe, 59, 313.
Humus, fungus flora and, 130.
Ion exchange—
isoelectric point and, 323.
mechanism of, 315.
Iron—
humates, 59.
isoelectric phospho-silicates, 69.
Irrigation—
aluminum in, water, 210.
calcium in, water, 210.
effect on—
availability of phosphorus, 214.
soil reaction, 212.
iron in, water, 210.
water for rice, 209–212.
Isoelectric—
point and ion exchange, 323.
precipitates of colloids, 57–77.
Lemna major, stimulation of, by organic matter, 299.
Lettuce—
sensitivity to aluminum toxicity, 270.
soils, phosphorus in, 181.
Lime, effect on—
dextrose decomposition, 142.
plasticity of soils, 293.
Löhnis, Felix, an obituary note, 333.
Magnesium, replaceable, 26.
Manganese—
determination of, in soil, 175.
relation to plant injury from soil acidity, 205.
Manure—
acids volatile, losses from, 354.
ammonia losses from fermenting, 354.
barley experiments with, 468.
carbon losses from, 354.
composition of, with respect to nitrogen, 335.
effect on—
nitrification, 474.
tillering of barley, 472.

farm, conservation and availability of nitrogen in, 335–363.
liquid, storage of, 338.
nitrogen—
availability of, under field conditions, 467–481.
conservation of, 337.
recovery in crops, 345.
reaction of cow, 351.
storage of, changes produced, 350.
Microörganisms, soil, phosphorus assimilation by, 431–436.
Mineralogical interpretation of rock analyses, 259.
Moisture-equivalent in soils, 370–376.
Molds, phosphorus assimilation by, 431; *see* also Fungi.
Mycorrhiza, 80.
Natrolite, base-exchange in, 41.
Nitrate—
data for different cropping conditions, 288.
nitrogen in—
soil fallow, 284, 471.
soils treated with various organic materials, 423.
Nitrates—
in market-garden soils, 281.
statistical methods in studying, 282.
Nitrification—
chemical nature of, 379.
in soils, 379.
on—
fallow soil, 474.
manured soil, 474.
Nitrite fomation as affected by anions, 380.
Nitrogen—
ammonia in—
fluid cultures of Azotobacter, 228.
manure, 351.
availability of, in farm manure, 335, 339.
effect on Azotobacter growth and N fixation, 219, 226.
fixation by Azotobacter, 219.
losses of, in handling manure, 338.
materials, decomposition of, by fungi, 147.
nitrate, under fallow and crops, 284.
recovery from crops, 345.
Nucleic acid, effect on N fixation by Azotobacter, 226.
Nutrient solution—
lettuce grown in, 268.
sand cultures for, 236.
Oats, as affected by manure, 344.
Organic—
carbon in soils treated with various organic materials, 421.
materials, composition of, 418.
matter—
accumulation in soils, relation to C:N, 413.
determination of soil, 483–486.
Lemna major, stimulation of, by, 299–309.
method of calculating average, content, 249.
temperature relationship in the E. United States, 247–252.
nitrogen in soils treated with various organic materials, 420.
Peptone, changes produced in, by Rhizobium, 389.
Permutite, X-ray pattern of, 40.
Phenylalanine, changes produced in, by Rhizobium, 397.
Phosphates—*see* also Soil phosphorus, phosphate, Soils phosphate.
acetic acid extract of, 445.
availability of soil, 448, 455.
citric acid extract of, 442.
exchange of, with humate ions, 77.
extraction with acids, relation to pH, 441.
hydrochloric acid extract of, 442.
oxalic acid extract of, 442.
percolation method of extracting, 449.
size of particles and amount of, 457.
soil, chemical method for estimating availability, 437–466.
solubility of, with various solvents, 455, 459.
toxicity of, 12.
Phosphorus—
assimilation of, by soil microörganisms, 431.
availability of, in irrigated soils, 209.
method—
comparison of, 178.
determining, in soil, 175.
Photosensitized oxidation of ammonia, 379.
Plant—
growth—
aluminum toxicity to, 267.
factors affecting, in acid soils, 183–207.
injury from soil acidity, 190.
pathogens, manual of, 80.
Potassium—
nitrate—
changes produced in, by Rhizobium, 401.

effect on nitrogen fixation by Azotobacter, 226.
Ragweed, C-N ratio in, 418.
Rhizobium, *see* Bacteria legume.
Rice soils, availability of phosphorus in, 209.
Rocks—
chemical changes during weathering of, 255.
weathering of in tropics, 254.
Rothamsted field data analyzed, 117.
Sand cultures, apparatus for large, 235–241.
Scolecite, base-exchange in, 41.
Sesquioxide-soil colloid systems, 71, 159.
Silica as photosensitizer in ammonia oxidation, 383.
Silicate, replacement of ions, by humates, 77.
Silica-sesquioxide ratio, relation to—
base-exchange capacity, 110, 166, 320.
soil acidity, 159–173.
Sodium—
humate colloids, preparation of, 58.
nitrate, effect on nitrogen fixation by Azotobacter, 226.
Soil—
a textbook on, 83.
acidity, nature of, as affected by SiO_2-R_2O_3 ratio, 159–173; *see* also Soils acid, reaction, H-ion concentration, Lime.
analyses from mineralogical data, 254.
apparatus for sampling, 1–3.
buffer power of the, in relation to solubility of phospate, 440.
Cecil clay, description of, 185.
Cecil clay loam, description of, 185.
Cecil sandy loam, description of, 185.
Colby silt loam, description of, 185.
colloids—*see* also Colloids.
ammonia method for characterizing, 93–97.
as affected by grinding, 28.
base-exchange of, as affected by grinding, 28.
Cecil, nature of, 43.
fusion analysis of, 31.
silica-sesquioxide ratio, review of literature on subject, 159.
colloids, silica-sesquioxide ratio, relation to—
acidity, nature of, 159.
base-exchange capacity of, 110, 320.
Cory silt loam, description of, 185.
fallow—
nitrate nitrogen in, 284, 471.
nitrification in, 474.
forming processes—
in the Hawaiian Islands, 253–265.
in the tropics, a monograph on, 243.
mineralogical point of view, 253–265.
weathered shells and rock analyses to illustrate, 254.
fungus flora of the, 123–158; *see* also Fungi.
Greenville fine sandy loam, description of, 185.
Greenville sandy loam, description of, 185.
Grundy silt loam, description of, 185.
manganese determination in, 175.
Miami silt loam, description of, 185.
microörganisms, *see* Microörganisms.
moisture penetration, method of studying, 1–3.
Norfolk sandy loam, description of, 185.
organic matter, *see* Organic matter.
oxidizing and dissolving, 175.
phosphate—*see* also Phosphorus, Phosphates.
chemical method of determining availability, 437.
solubility of, in various solvents, 459.
phosphorus determination in, 175;—*see* also Phosphorus, Phosphates.
plastic range of the, 369.
profile, plasticity studies of the, 294.
properties, single-valued, 365–378.
reaction, as affected by irrigation, 212; *see* also Acidity.
rolling out limit of, 369.
sampling with a compressed air unit, 1–3.
science—
fundamentals of, 79.
textbook, 84.
solution—
aluminum concentration in, affecting plant growth, 183.
calcium-potassium ratio in, 198.
H-ion concentration of, affecting plant growth, 183.
sticky-point in, 369.
Susquehanna fine sandy loam, description of, 185.
type, flow-plasticity as related to, 295.
Soils—
a handbook of, 81.

acid—*see* also H-ion concentration.
decomposition of dextrose in, 142.
plant growth in, 183.
ammonia interaction with, 95.
base-exchange, *see* Base-exchange.
base saturation of, determination of, 99, 205.
Hawaiian, mineralogical composition, 253–265.
irrigated, availability of phosphorus in, 209–218.
lettuce, phosphorus in, 181.
market-garden, sampling for nitrates, 281–290.
mechanical analysis of, by hydrometer method, 85–92.
modeling of, an aid in their study, 487–489.
nitrification in, 379–384.
organic matter in, *see* Organic matter.
phosphate—*see* also Phosphorus, Phosphates.
extraction of, by acids, 458.
supplying power of, 457.
Wrangell's work on, 459.
photochemical oxidation in, 382.
plasticity of, 291–298.
rice, water soluble phosphorus in, 213.
saturation of, as factor of plant injury, 205.
sticky-point of, 295, 369.
tomato, manganese and phosphorus in, 180.
tropical, monograph on, 243.
Sticky-point, determination of, 369.
Stilbite, base-exchange in, 41.
Straw—
effect on manure storage, 357.
C-N ratio in, 418.
Uranium salts as photosensitizer in ammonia oxidation, 383.
Urea—
changes produced in, by Rhizobium, 388, 399.
effect on N fixation by Azotobacter, 226.
Urine, reaction of cow, 351.
Wood-fiber, C-N ratio in, 418.
X-ray—
analysis to determine base-exchange, 25–55.
permutite pattern, 40.
studies on zeolites, 40.
Zeolites—
base-exchange in, 25, 39.
X-ray studies on, 40.
Zinc as a photosensitizer in ammonia oxidation, 383.

SOIL SCIENCE

Manuscripts submitted for publication and communications concerning editorial matters should be sent to Dr. Jacob G. Lipman, New Jersey Agricultural Experiment Station, New Brunswick, N. J., U. S. A.

Correspondence concerning business matters should be addressed to The Williams & Wilkins Company, Publishers of Scientific Journals and Books, Mount Royal and Guilford Avenues, Baltimore, U. S. A.

Twenty-five reprints, without covers of articles will be furnished gratis to contributors when ordered in advance. A table giving cost of additional reprints, with an order slip, is sent with proof.

SOIL SCIENCE is issued monthly. Each issue consists of approximately 85 pages at present. Two volumes a year are issued at present. Each volume consists of approximately 500 pages.

Subscription price: $5.00 per volume in the United States and countries within the Postal Union. $5.50 outside the Postal Union.

Claims for copies lost in the mails must be received within 30 days (domestic), and 90 days (foreign), of the date of issue. Changes of address must be received at least two weeks in advance of issue.

New subscriptions and renewals are entered to begin with the first issue of the current volume. Should any issue of the current volume be out of print at the time the subscription order is received, the pro-rata value of such numbers will be credited to the next volume, and the renewal invoice therefore adjusted accordingly.

Subscriptions should be renewed promptly—To avoid a break in your series, subscriptions should be renewed promptly. The publishers cannot guarantee to supply back issues on belated renewals.

Subscriptions, new or renewal, should be sent to the Publishers or to Agents listed below.

Index for Volumes I–XXV is available at $3.00 so long as present supply lasts.

AGENTS

For Argentina and Uruguay: Beutelspacher y Cia, Sarmiento 815, Buenos Aires.

For Australia: Angus & Robertson, Limited, 89–95 Castlereagh Street, Sydney.

For Belgium: Henri Lamertin, 58 Rue Coudenberg, Bruxelles.

For the British Empire, except Australia and Canada: Baillière, Tindall & Cox, 8 Henrietta St., Covent Garden, WC. 2, London, England.

For Canada: Wm. Dawson & Sons, Ltd., 91 Queen Street East, Toronto.

For China: Commercial Press Ltd., Paoshan Road, Shanghai, China.

For Denmark: H. Hagerup's Boghandel, Gothersgade 30, Kjöbenhavn.

For France: Emile Bougault, 48 Rue des Ecoles, Paris.

For Germany: B. Westermann Co., Inc., Zimmerstrasse 35–41, Berlin SW-68, Germany.

For Holland: Scheltema & Holkema, Rokin 74–76, Amsterdam.

For Japan and Korea: Maruzen Company, Ltd. (Maruzen-Kabushiki-Kaisha), 6 Nihonbashi Tori-Nichome, Tokyo; Fukuoka, Osaka, Kyoto, and Sendai, Japan.

For Spain: Ruiz Hermanos, Plaza de Santa Ana, 13, Madrid.

THE WILLIAMS & WILKINS COMPANY

Publishers of Scientific Books and Periodicals

BALTIMORE, U. S. A.

PUBLISHERS OF: *Medicine, Journal of Urology, Journal of Pharmacology and Experimental Therapeutics, American Journal of Tropical Medicine, Journal of Immunology, Journal of Industrial Hygiene, Quarterly Review of Biology, Journal of Bacteriology, Annals of the Pickett-Thompson Research Laboratory, Journal of Biological Chemistry, Chemical Reviews, Journal of Dairy Science, Soil Science, Social Forces, Personnel Journal, Journal of Comparative Psychology, Mental Measurement Monographs, Studies in Psychology and Psychiatry, Occupational Therapy and Rehabilitation, Child Development, Journal of Aviation Medicine, Journal of Clinical Investigation, The American Journal of Clinical Pathology.*

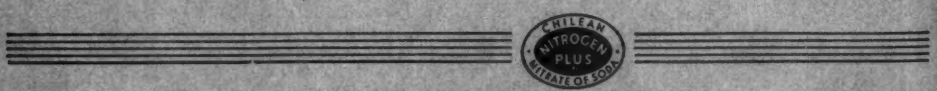
Why Chilean Nitrate is "Nitrogen PLUS"

THE mighty forces of Nature all combined to make Chilean Nitrate the superior nitrogen fertilizer. It is the natural nitrate, the good old "Soda" upon which the successful farmer relies for paying crops of cotton, corn, grain, fruit, truck.

Due to its natural origin, it contains rare elements—iodine, boron, magnesium, etc. Science has learned that these rare elements, once considered unimportant in plant growth, actually are of tremendous value. They are plant foods in themselves. Combining with its nitrogen, they make Chilean Nitrate a super-nitrate . . . Nitrogen PLUS. This explains the never-failing superiority of Chilean Nitrate in official tests and in the experience records of practical farmers.

Chilean increases yield and quality so effectively that it pays back its small cost . . . then pays a good profit too. It is often the difference between big success and profitless crops.

Special crop data will be furnished free on request. Many booklets and bulletins at your disposal. Write.

Chilean
Nitrate of Soda
EDUCATIONAL BUREAU
57 William Street, New York, N. Y.

Scientifically trained, practical men represent the Bureau throughout the country